Use of latex in natural fibre reinforced plastics

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Master thesis
August 2000

Preface

This report was written as a graduate paper for the Faculty of Aerospace Engineering, Delft University of Technology and describes the result of one year of research for the Center of Lightweight Constructions (CLC), at the Structures and Materials Laboratory.

I would like to thank everyone who helped me during the last year. A special thank to Ir. W.D Brouwer, my supervisor, Prof. Ir. A.Beukers, Prof.Dr.Ir.J.J.Elmendorp and Dr.Ir. H.E.N. Bersee for taking a place in my examination committee. Thanks to everyone who proof-read my report, answered questions or helped me during my test work.
Also thanks to my friends, girlfriend, sister and parents for their support pep-talks and necessary distraction.

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Abstract

Polymers and composite materials have replaced many conventional materials (wood, metals, natural fibres) in the past decades. Cost reduction, productivity increase, weight saving and better mechanical properties are the main reasons for this development.

In recent years however, there is a renewed interest in natural fibres, especially as reinforcement in composite materials. Main reasons for this is an increased awareness of our environment. Typical subjects in this respect are 'reduction of CO_2 emissions', 'recycling' and 'protection of resources' . The automotive industry was the first to use natural fibres on a larger scale, not only because of environmental advantages but also because of cost- and weight reduction. Several cars produced or even used at this very moment, contain a considerable amount of natural fibres.

This report investigates the possibilities of natural fibres as reinforcement in thermoplastic composites. It focuses on the problems of natural fibre prepreg production and brings up latex processing as a possible solution to some of these problems.

Natural fibres can be classified into three categories: leaf-fibres, seed-hair fibres and bast fibres depending on their position in the plant. Bast fibres, like hemp, jute and flax, show the best mechanical properties. These fibres in fact are composites in themselves, consisting of ultimate fibres made out off cellulose and hemicellulose in a matrix of lignin, surrounded by pectin.

They can be removed from the plant stem by a process called retting. In average they have a tensile strength of 500 MPa, Young's modulus of 28 GPa and density of 1.5 g/cm^3.

The first composites entering the automotive industry were glass reinforced thermosets (polyester, epoxy). In the late eighties, the first glass reinforced thermoplastics were introduced. They offered better impact resistance, weight reduction, unlimited shelf life and reduced cycle times. Main disadvantage of thermoplastics is the high viscosity of the melt, which makes impregnation of fibres difficult. There are several impregnation techniques: solution processing, melt impregnation, film stacking, filament bundle coating, commingling, slurry processing and dry powder prepregging.

Natural fibres are an interesting alternative to glass fibres in composites. They offer a high specific stiffness and are non abrasive, renewable and cheap. Lower strength, restricted processing temperatures, variable quality and price and moisture absorption are the main disadvantages. Slurry processing seems to be an interesting alternative to produce natural fibre prepreg material.

A special class within slurries are the latices. They can be defined as stable colloidal dispersions of a polymeric substance in an aqueous medium. Typical applications are paints, non-woven binders, carpet backing and paper coatings. Some latices are only used as a semifinished product in the production of polymer granules. Examples are ABS and PVC.

Latices till now have never been used as matrix material in composites although they could offer certain advantages over other composite processing techniques: no unpleasant solvents are used, viscosity is low compared to polymer melts and solid content is much higher than for polymer solutions. ABS, PVC and HIPS (High impact polystyrene) latices are very interesting for natural fibre composites prepreg processing. They are, however, hard to obtain.

Two different latex types have been used to impregnate a random flax fibre mat: ABS and Acrylonitrile acrylic (AN 12DE). Tests showed that latex particles in ABS are small enough not to be filtered out by the mat structure. To achieve an even distribution of the particles in the mat at exceptable speeds, additional pressure was applied by squeezing. Drying is an important aspect in latex prepregging. Latex can form a film at the surface that hinders water evaporation. In the final prepreg the film is desired however, because it prevents polymer powder from falling off. Particle migration to the surface is another aspect that has to be minimized.

Flexural test were done on both AN 12DE/Flax and ABS/Flax laminates. The reinforcing effect of the fibres on flexural strength was limited in the case AN 12DE , because of bad fibre/matrix interaction. Flexural modulus was raised by a factor 3 (9.5 GPa). No considerable weight saving is possible compared to a polyester/glass composite.

ABS/flax laminates were 3.5 times as strong (119.4 MPa) and 7 times as stiff (7.3 GPa) as unreinforced ABS. Weight savings are possible (compared to ABS/glass composites), especially if the bad quality of the ABS latex used in this experiment is considered.

A good bond between fibres and matrix is essential to obtain a good composite that uses the full potential of the reinforcing fibre. Compatibility of the hydrophilic natural fibres and hydrophobic synthetic thermoplastics is bad. Sizing can be used to improve compatibility.

Maleic Anhydride modified PP (MAPP) is a well- known sizing for PP composites. Two types of MAPP emulsions were tested: Permanol 603 and AAP5. The latices were easy to apply and improved flexural stress by 21% for Permanol treated laminates and 12 % for AAP5 treated laminates. The maximum mechanical properties were obtained at 1% Personal 603 and 2 % AAP5 content. Deviation of these amounts can lead to a decline of properties below those for untreated laminates.

Sizing emulsions like MAPP could be mixed with ABS latex so that fibre sizing and fibre impregnation by the matrix is integrated in one step. Suitable ABS sizing for ABS could not be obtained within the framework of this research.

Latex prepregging on an industrial scale is possible. Transport and storage offer no problems as long as latices are not frozen or exposed to excessive heating. Impregnation can be done by pouring latex over the mat or by passing it through a latex bath. IR and dielectric heating devices are in theory the most suitable for drying the prepreg.

Symbols and Abbreviations

List of symbols

a = radius of the particles [mm]

γ = surface free energy of the polymer particle [mN m^{-1}]

γ_{sv} = solid/vapor interfacial energy [mN m^{-1}]

γ_{sl} = solid/liquid interfacial energy [mN m^{-1}]

γ_{lv} = liquid surface tension [mN m^{-1}]

e_1 = electrical charge particle 1 [C]

e_2 = electrical charge particle 2 [C]

E_m = matrix modulus of elasticity [GPa]

E_c = composite modulus of elasticity [GPa]

E_f = modulus of fibre material [GPa]

$E_{f,eff}$ = effective fibre modulus [GPa]

$E_{f10\text{-}40}$ = flexural modulus [GPa]

$E_{f10\text{-}40,spec}$ = specific flexural modulus [GPa]

F = force [N]

F_{cf} = capillary forces [N]

F_{st} = surface tension forces [N]

F_w = deformation resistance [N]

F_c = coulomb forces [N]

G_f = composite fibre content by weight [-]

K = constant [-]

M_w = molecular weight [-]

p = fibre perimeter [-]

Θ = half-angle of coalescence [radians]

η = polymer viscosity [Pa s]

r = particles center distance [m]

t = time of coalescence [s]

T_m = melt temperature [°C]

V_f = fibre volume fraction [-]

V_m = volume fraction of the matrix [-]

W_a = work of adhesion [J]

W_d = dispersive forces [J]

W_p = polar forces [J]

W_h = work done by polar forces [J]

W_{ab} = work done by acid-base interaction [J]

σ_m = ultimate matrix stress [MPa]

σ_c = ultimate composite stress [MPa]

σ_f = ultimate fibre stress [MPa]

σ_{flex} = maximum flexural stress [MPa]

$\sigma_{flex,spec}$ = specific maximum flexural stress [MPa]

Θ = contact angle [°]

Abbreviations

ABS = Acrylonitrile -co- Butadiene -co -Styrene

ABSF = laminates of flax mat reinforced ABS

AN 12DE = Acronal 12 DE

ANF = laminates of flax mat reinforced Acronal 12 DE

HIPS = High impact Polystyrene

NFRP = Natural Fibre Reinforced Plastics

PMMA = Polymethylmethacrylate

PP = Polypropylene

PVC = Polyvinyl Chloride

SAN = Styrene-co-acrylonitrile

TPC = Thermoplastic Composite

Table of content

Introduction

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In recent years however, there is a renewed interest in natural fibres, especially as reinforcement in composite materials. Main reasons for this is an increased awareness of our environment. Typical subjects in this respect are 'reduction of CO_2 emissions', 'recycling' and 'protection of resources' . The automotive industry was the first to use natural fibres on a larger scale, not only because of environmental advantages but also because of cost- and weight reduction. Several cars produced or even driving at this very moment, contain a considerable amount of natural fibres.

Two years ago, the Center of Lightweight Constructions (CLC) started the 'Biolicht project' together with several other companies (ATO, Wientjes Emmen, CERES, KIEM, Focwa/Cintec). The objective of the 'Biolicht Project' was to determine the possibilities of renewable raw materials in light weight, semi-finished materials and products for the transport sector. This report describes part of the research done in the last two years.

It focuses on the use of natural fibres in thermoplastics and brings up latex processing as a possible process method for this new type of composite material.

The reports starts with a short review on available natural fibres, their structure and mechanical properties (chapter 1) . The importance of fibre reinforced thermoplastics in automotive industry is discussed in chapter 2, a description of thermoplastic composites production techniques is given and the role natural fibres can play in this application is explained.

Latices can be used in the production of natural fibre reinforced plastics (NFRP's). Chapter 3 describes the nature of the latices and explains why they are so interesting. Several impregnation and mechanical property tests were done using a flax mat and two different latices (Chapter 4 and 5). The interaction between fibre and matrix in NFRP's is bad. Chapter 6 how this interaction was improved using two different fibre emulsion sizings.

Chapter 7 describes the opportunities of latex prepreg processing on an industrial scale.

The report ends with conclusions and recommendations.

1. Natural fibres

There are many natural fibres with interesting characteristics and properties.
A classification of the fibres is given in section 1.1. Structure and mechanical characteristics are given in section 1.2 and 1.3. Chapter 1 concludes with a discussion of the different processing steps of natural fibres (1.4)

1.1 Important natural fibres

Natural fibres occur in many different parts of plants and execute different functions. This has a large influence on fibre characteristics, and therefore also on possible end-uses. There are many ways to classify natural fibres. The most popular classification is based on the position of the fibre in the plant [15]:

Leaf fibres:
Long strand leaf fibres give mechanical support to the leaves. They are composed of many small ultimate fibres, 12 mm long and a diameter around 30 µm. The fibres are coarse and therefore used as cordage, mats rugs and carpet backings. Manila hemp (abaca) and sisal, used for twines and ropes, are the most famous fibres in this class.

Seed-hair fibres:
Hair fibres are found on the seeds or on the inner walls of fruit. They are attached to the seeds of some plants for aid in wind dispersal. A hair consists of a single long narrow cell which is the ultimate fibre. These fibres have large lengths (20 mm) and small diameter (20µm). Cotton and kapok are the most important fibres in this class. They are used in many textile applications.

Bast fibres
Bast fibres exist in the inner bark or phloem of many plants to provide structural rigidity to the stem. In general, bast fibres have lengths of 100 cm and widths less than 1 mm. The ultimate fibres range in size. Flax, hemp and ramie have extremely long ultimate fibres with aspect ratios of 1000 and more. Because of their softness bast fibres are also called soft fibres.

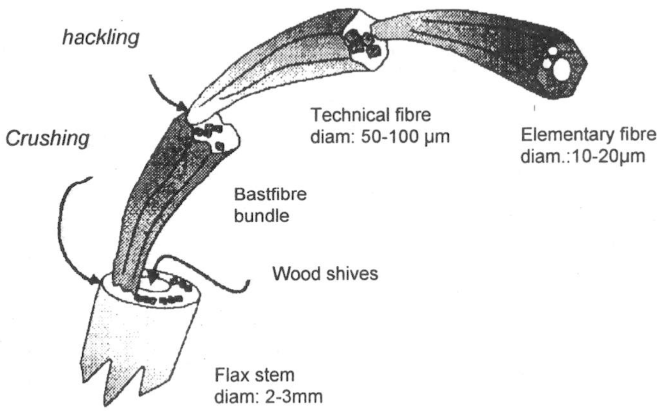


Figure 1.1: Structure of a flax fibre

Bast fibres are used in many textile applications.

1.2 Bast fibre structure

A bast fibre is an inhomogeneous material, build up from many different chemical components. The share of each component depends on fibre type, age, climatic conditions, test method, etc. This is the reason for the large variation in data on fibre composition (see table 1.1).

Cellulose is the basic structural component of all plant fibres. It consists of glucose units that are linked together in long chains, which in turn are linked together in bundles called microfibrils. The estimated tensile strength for these fibrils is very high: 7.5GPa. Cellulose therefore is the component that gives natural fibres strength.

The cellulose fibrils are bonded together into elementary fibres (see figure 1.1) by hemicellulose, consisting of polysaccharides bonded together in relatively short, branching chain. Because of its hydrophilic character, water absorption of hemicellulose is high.

The ultimate fibres are bonded vertically into long chains (technical fibres) by lignin, a amorphous short-chain polymer that gives rigidity to the plant. Several technical fibres are bonded horizontally by lignin, forming a bundle. Each plant stem contains several bundles. During a process called retting (see 1.4), the pectin is attacked and the bundles can be removed from the plant.

Source: P.O Olesen and D.V Plackett

Fibre	Cellulose	Hemicellulose	Lignin	Pectin
Flax, hemp	68-85	20-31	3-5	5-10
jute	70-75	10-17	1	1
cotton	89-99	12-15	-	-
coniferous wood	39-45	30-33	22-28	-

Table 1.1: Chemical composition of some natural fibres

1.3 Mechanical characteristics

All natural fibres are in fact composite materials with different combinations of cellulose, hemicellulose, pectin and lignin. Every combination results in different mechanical characteristics and limits the possible application fields.

Table 1.2 lists mechanical characteristics of some important natural fibres and for some synthetic fibres in comparison.

Sources: Buijs, 1991; Rowell, 1997; R.Brouwer, 2000

Fibre	**Density (g/cm^3)**	**Tensile Strength (MPa)**	**Young's modulus (GPa)**	**Elongation at break (%)**
Bast fibres				
Flax	1.5 -1.52	351-900	28.5-110	2-3
Jute	1.4 – 1.5	400-900	24.1-26	1.5
Hemp	1.48	550-900	25-29.5	3.5
Leaf fibres				
Sisal	1.45-1.5	507-524	16.7-17	2-3
Palm	1.4-1.5	545-578	13.7-15	3
Henequin	1.49-1.5	537-580	12.8- 13.6	3.5-5
Seed-hair fibres				
Coir (husk)	1.5	213-270	23.7	16
cotton	1.5	400	12	3-10
Synthetic fibres				
E-glass	2.54	3500	73.8	3
S-glass	2.48	4600	88.6	3
Aramid	1.45	2700	130	2.5
Carbon	1.76	3300	225-255	1.5

Table 1.2: Mechanical properties of natural-and engineering fibres

The given values show large fluctuations. The reasons for this are:

Variety of species; There are many different varieties within one species. They all differ in composition and characteristics.

Growing conditions; growing conditions like location, types of soil, amount and type of fertilizer applied, moisture and temperature, influence the chemical composition of plants.

Processing aspects; there are several methods to extract the fibers from the plant (see section 1.4). They have a large influence on the final fibre quality. During processing of the fibres into mats, yarns and woven, failures can be introduced in the fibres that have a negative influence on final properties

Test method; there are several standards to obtain mechanical data that all give different results. An important difference originates from different grip distances in a test to obtain tensile properties. If a large grip distance is used, the chance for irregularities, that can cause fracture in the natural fibre, is higher. In the case of glass fibres, the grip distance is of minor importance because this man-made fibre has fewer flaws.

The density of all natural fibres is around 1.5 g/cm^3. Glass fibres are much heavier. This will turn out to be the main reason why natural fibres can be an interesting alternative for glass in composite structures (see chapter 2).

Bast fibres have the highest tensile strength of all natural fibres. Synthetic fibres however, are between 4-9 times stronger. Here natural fibres are clearly in a disadvantage.

Bast fibres also show the highest stiffness of all natural fibres. Stiffness of glass fibres however is three times higher, and carbon fibres even 8 times higher. Elongation at break is equal for almost all types of fibres.

1.4 Natural fibre production chain

The Life Cycle for natural fibres generally consists of four major steps, as can be seen in figure 1.2. They will be discussed in this section.

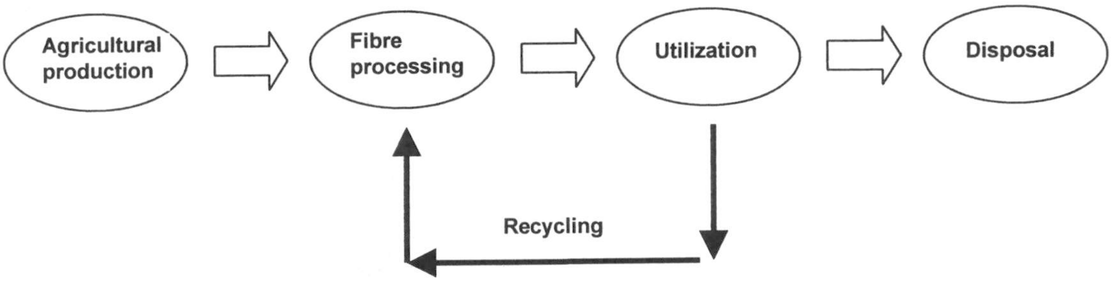


Figure 1.2: Life cycle of natural fibres

1 Agricultural production

Agricultural production involves breeding, seeding, growing and harvesting of the fibres. Important factors that determine final fibre quality are weather conditions, soil preparation, the amount and kind of fertilizers and pesticides used, etc. In the last decades, efficiency and quality have been optimized by developing new fertilizers and harvesting machines. Further quality improvement could be achieved by breeding new fibre crops. Several institutes are working on this (ATO in Wageningen, Holland for example).

2 Fibre processing

Fibre processing involves all the necessary steps from the extraction of the fibres from the plant to the final processing of these fibres into wovens and non-wovens. Especially the first activity in this process, retting (fibre extraction), has a major influence on fibre quality. During the retting process the stems are submitted to the action of water, fungi and bacteria. The water softens the plant and creates an environment in which fungi and bacteria flourish. The bacteria enter the stem and start breaking down the pectin that surrounds the fibre bundles. Eventually also the matrix that holds the fibre cells together in the bundle will be broken down. It is the trick to stop the process before this happens. Several different retting techniques are being used:

Dew retting is the oldest and cheapest retting technique. After harvesting the plants are spread on the field and left there for three to seven weeks to undergo microbiological attack.

During this period the plants have to be turned once in a while to get a proper ret. Dew retting has many disadvantages. The retting can take a long time depending on the weather conditions. During this period land is occupied that can not be used for any other purposes. The biggest disadvantage however is the bad control over the process. This is why the process is only used for plants that were rejected for water retting because of their bad quality.

Water retting is used for better quality plants. They are retted in rivers or ditches or in tanks that were specially designed for this purpose. Retting in rivers or ponds can take between two and three weeks depending on the speed of flow, weather and water temperature. To get better control over the retting warm-water retting was introduced. Warm water retting takes place inside a special equipped rettery so the costs are higher compared to retting in cold water. There are however some important advantages: There is less time needed for the retting process and the increased process control results in better quality fibres.
Drawbacks of the method are the emission of bad smell and pollution of water.

New techniques have been developed with the following objectives in mind:

- Reduction of harvest risks due to the retting process
- More constant fibre quality
- Better fibre quality
- Cost reduction
- Reduction of pollution
- Reduction of parties involved in the process

Duralin process: Ceres BV (Holland) has developed a process derived from the PLATO process that is used for wood. Ceres made this process suitable for processing harvested straw that has not yet been retted. The process is based on three steps:

1: hydro-thermolysis, in which the fibres are brought to a temperature of 200 degrees Celsius under a pressure of 14 atm. The hemicellulose and lignin chains depolymerise into aldehyde and phenol groups.
2: drying, during which the obtained depolymerised fibres are dried.
3: curing which the aldehyde and phenol groups react, thus forming a waterresistant bakelite like structure. The flax fibres treated in this way are called Duralin flax and have a better and more constant quality than untreated, green or dew retted flax fibres:

- Low moisture absorption with reduced swell
- Strongly reduced risk of rotting and degradation
- No retting process required, reducing the risk of harvest losses

The process only needs energy and water. Most of the energy can be obtained from the by-products.

Reutlingen steam explosion process: This process is based on the steam explosion process that was patented in 1930 and used to extract fibres from agricultural waste. The Institut für Angewandte Forschung (IAF) in Reutlingen made it suitable for treatment of hemp, flax and jute fibres. The process consist of three steps:

Step 1: decorticated fibre bundles are impregnated with NaOH at a concentration range of 0.1-0.5 % at different temperatures (20-120 degrees Celsius) in a reaction chamber.
Step 2: The material is subjected to saturated steam for a desired time. At the end of the steam treatment, the material is exploded into a cyclone.
Step 3: The degraded materials, like pectin, hemicellulose etc. are extracted by an alkaline scouring.

This treatment results in a fibre with high fineness and a superior yield of good quality-fibre.
The process can be tailored for different raw materials and different applications. Therefore also raw materials with different levels of retting can be used. Further processing can be done on standard machinery.

Enzymatic retting: This process is similar to warm- water retting. The difference is the use of specific enzymes that makes a more controllable and accelerated retting possible. The result is a high yield and a fibre with a lighter color and higher spinning performance.
The enzyme-solution can be recycled. The costs involved in enzymatic retting are high compared to dew-retting.

Green flax extraction process: In this process the retting step is omitted. After harvesting and deseeding the flax is broken in a specially designed breaker. Then the fibres are scutched and hackled on a machine specially designed for this process. The result of this step is a fibre that can be spun into a yarn. Green-flax, when properly prepared, is stronger than retted flax. A disadvantage is that a severe scutching is needed to clean the fibres. This results in a higher amount of short fibers compared to retted flax. The advantages of this process are that no unpredictable retting process is needed and all the processing can take place in one company.

After the fibre is chemically released from the stem, the fibres are removed from the stem by a mechanical process called scutching and hackling. The most important end product is the valuable long fibre, by products are short fibres , shives (woody flax core) and hurds (woody hemp core)

Utilization

In 1999/2000 , 74000t flax long fibres, 83000t flax short fibre and 34000t hemp short fibre were produced in the EU and used in several applications [8] (see appendix A for more detailed information).

The long flax fibres are traditionally used in fashion products (linen) and other textiles. These are products with high added value. There is however a severe competition with synthetic fibres in this market, that is very depending on fashion trends.

Short fibres are mainly used in pulp for paper making. This is a high volume market with low added value (see appendix A). Other applications are ropes, geo textiles and packaging materials. Due to a strong competition of fibres from Asia and Eastern Europe, farmers were forced to search for new applications with a good market volume and better prices. This lead to the development of two interesting new applications [13]:

1. Automotive industry; natural fibres are used as reinforcement in composite materials for car interior parts (see Appendix B). In 1999, more than 21000 t fibres were used in this sector. This development is discussed in chapter 3.
2. Ecological thermal insulation materials; this is a growing market that expect to sell several 10000 ton's a year in 2005.

Despite these new developments, profit margins are still small. Without EU subsidies it is even impossible to survive in this sector. Therefore even more effort has to be done to find new applications and make new processing techniques profitable.

4 Disposal

When a fibre product has reached the end of its lifecycle, there are two possibilities: recycling and disposal. Natural fibres are normally recycled into low grade products. The use of old textiles for pulp is a good example. Composites used in the automotive industry could be shredded and used in injection molding. Disposal can be done by composting or burning. Burning of natural fibres is easier than of glass fibres, which is an important advantage for natural fibres in composites (see section 2.5).

2. Fibre reinforced thermoplastics

Thermoplastic Composites (TPC's) are used in many applications where weight saving and productivity are an issue. This chapter starts with a short introduction into composite materials (2.1). In section 2.2 the role of these composites in automotive industry is explained. Section 2.3 explains why TPC's are gaining importance over reinforced thermosets. There are several ways to produce TPC's. The advantages and disadvantages of these techniques are discussed in section 2.4. There is a growing interest in natural fibres as reinforcement in TPC's. Section 2.5 explains the reasons behind this development. Section 2.6 deals with suitable natural fibre prepreg processing techniques. Current applications of natural fibre reinforced plastics (NFRP's) are discussed in section 2.7

2.1 Introduction into composite materials

A composite is a material system made up of two or more material components. Goal is to combine different material characteristics in one structure. Straw reinforced clay is a good example. The straw gives strength to the material, while clay offers the possibility to keep it in the desired shape.

Modern composites consist of glass, carbon, or aramid fibres in a polymer matrix.
Both thermoset (epoxy, polyester, polyurethane) and thermoplastic (PP,PE, PEI, PEEK) matrices are used. In these materials, the fibres are responsible for strength and stiffness. The matrix is responsible for shape preservation, transmitting shear forces between the fibres and preventing fibre buckling. By choosing the right combination of fibre and matrix, a material can be designed with properties that fits the structure in which it is used.

In the last few decades, polymers have replaced many conventional materials (metals, wood) in various applications reaching from sport goods to space structures. The main reasons for this development were ease of processing, productivity increase, cost reduction and weight saving. There is a continuous development of new composite structures and processing techniques. Therefore composites are expected to enter more and different application areas in the future.

2.2 Fibre reinforced plastics in the automotive industry

The automotive industry has always been a driving force for new developments in composite design and processing techniques. The reason for this is obvious: The high costs involved in research and development can only be regained by an extensive use in a high volume market.

Composites offer good possibilities in this industry that is aiming at reduced costs, higher fuel efficiency, better recyclability and safety. Weight saving is a key factor in this development.

A study by Lovins (1996) describing an aerodynamic, low weight, hybrid- electric driven concept car showed that a weight reduction up to 67% was necessary to create a car that has three times the fuel economy of today's conventional cars. This can be realized by integrating several components into one new composite component.

The composites that first entered the automotive industry were based on thermoset matrices.

Manufacturing processes for these composites are [4,7,13,17]:

- Hand lay-up
- RTM (*resin transfer molding*)
- SRIM (*structural reaction injection molding*)
- SMC *(sheet molding compound)*

Hand lay-up involves the impregnation of fibrous material placed in a mould by means of a roller or brush. It is a very labor intensive method and only used for specialty products.

RTM involves the injection of a fibrous preform which is placed between a pair of matched moulds. This preform is impregnated by a thermoset resin by applying a pressure difference (4-8 bar) over the mould. In vacuum assisted RTM, pressure difference is obtained through applying vacuum over the mould.

SRIM is similar to RTM. Two highly reactive resin components are combined and injected into the mould with fibrous material. Curing time for SRIM resin are in general shorter than for RTM resins.

Figure 2.1: Alfa Romeo GTV Coupe hood, a typical SMC product

SMC involves the distribution of chopped fibres on a packaging film covered by a thermoset resin (i.e.polyester). After distribution, a second packaging film covered thermoset resin is placed on top of the first. The package is rolled to achieve impregnation. SMC products are made by cutting a desired piece from the SMC-prepreg, removing the packaging film, placing it in a mould and press it at elevated temperatures (140-170 degrees Celsius) to cure the thermoset.

The SMC process offers advantages like good surface quality (see figure 2.1) and controlled fibre orientation. Processing speeds are however limited to the curing time of the thermoset.

2.3 Development of thermoplastic composites

The first high volume application thermoplastic composites (TPC) was a 40% continuous glass mat reinforced polypropylene (GMT) for the 1976 Chevrolet Monza grill opening retainer (www.nottingham.ac.uk) In the 1980s they also entered the aerospace industry in the form of unidirectional carbon fibres in a PEEK matrix (named APC2, produced by ICI).
Later developments were reinforced polyetherimide (PEI) and poly(phenylene sulfide) (PPS).
In the automotive industry, glass mat reinforced thermoplastic (GMT), with mainly PP as a matrix, developed into a dominant high impact, structural material. Compared to metals, they provide higher strength-to –weight ratio, resistance to corrosion and electrical insulating properties. Compared to SMC, GMT not only offers reduced cycle times, but also greater shelf life, higher impact resistance, lighter weight and recyclability.

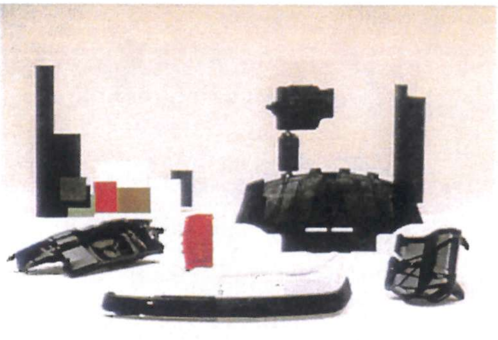


Figure 2.2: Typical GMT products

Main disadvantages are the absence of a class A surface finish and the fact that they can only be used for non structural and semi-structural parts due to limited fibre content.

GMT material normally consists of randomly oriented glass-fibres (same strength and stiffness in all directions). Sometimes other types of glass reinforcements are added to this material to improve certain characteristics:

- Unidirectional glass-fibre woven rovings to add strength and stiffness in one direction
- Long, chopped fibre glass-mats for better surface quality

Table 2.1 list some mechanical properties for fibre reinforced thermosets and thermoplastics. From this table it is clear that PP is not the only thermoplastic used in TPC. The popularity of PP in the automotive industry can be described to its low price and acceptible performance.

Source: derived from www.owenscorning.com

Polymer type	material	G_f (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
Glass mat reinforced thermoplastic							
	PP	20	57.2	3.59	44.8	3.72	3.0
	ABS	20	106.9	6.0	75.85	6.2	2.0
	SAN	20	131.0	7.6	100.0	8.6	1.8
	PBT	30	193.1	8.1	131.0	8.3	4.0
	PET	30	220.6	8.62	144.8	9.0	6.6
	Nylon 6	30	200.0	7.65	165.5	7.24	3.0
	PC	10	110.3	4.1	82.7	5.2	9.0
Glass fibre reinforced thermosets							
	Polyester SMC	20	110.3	9.7	36.5	11.7	0.4
	Polyester SMC	30	179.3	11.0	82.7	11.7	1.0
	Polyester SMC	50	310.3	13.8	158.6	15.65	1.7

Table 2.1: mechanical properties of thermoset and thermoplastic composites

2.4 Prepreg processing techniques

A prepreg is a semi-finished composite material in which fibre and matrix are combined. It can be shaped into the final product using a suitable pressing technique. Goal of prepreg processing is obtaining a consolidated prepreg in which each fibre is equally spaced apart and is wetted completely by the matrix (see figure 2.3). This prepreg is the best starting point for a homogeneous and void free composite material and requires less pressure and lower temperature during final product processing. They are easy to handle and offer the possibility to reduce cycle times.

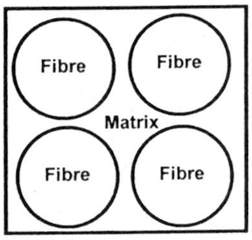


Figure 2.3: Ideal composite structure

There are several prepreg processing techniques that try to achieve the situation in figure 2.3 including [4,6,7,13,17]:

- *Solution processing*
- *Melt impregnation*
- *Film stacking*
- *Filament bundle coating*
- *Commingling/ Co-weaving*
- *Slurry processing*
- *Dry powder prepregging*

These techniques will be shortly discussed in the following.

Solution processing:

Solvents can be used to lower the viscosity of the thermoplastic to such an extent that it can impregnate fibres at room- or little higher temperature. When impregnation is completed, the solvent is removed by drying (see figure 2.4).

Because of their high molecular weight, only low concentration solutions (max 15%) can be realized. This makes it difficult to deposit enough matrix material onto the fibres. Thermoplastic solutions, even in low concentration solutions (3-6% by weight), are jelly-like. Therefore pressure is still needed to achieve good impregnation. It is difficult however to fully remove the solvent from the prepreg. The remaining solvent is responsible for voids in the prepreg, the escaping solvent for bubbles on the surface. These can however partly be removed during consolidation under pressure.

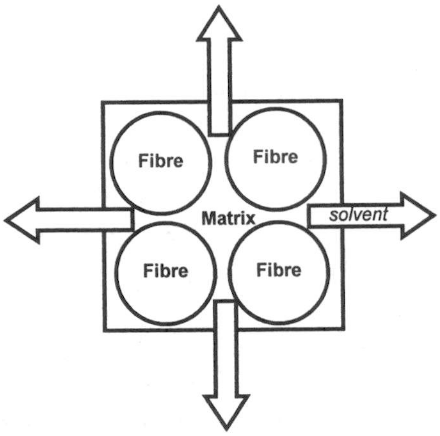


Figure 2.4: Solvent processing

The solvents used in this process are not very popular from an environmental point of view. They can be dangerous to workers' health and thus care has to be taken in avoiding solvent emission. This makes expensive processing equipment necessary. The process is only used for engineering plastics in special areas like space and aerospace. A good example is Cetex, a thermoplastic composite with PEI matrix produced by ten Cate (Nijverdal, Netherlands)

Melt impregnation

Melt impregnation is one of the most important methods to produce thermoplastic prepregs. In this process, a thermoplastic melt is deposited on the passing fibres by an extruder. In the next step the prepreg enters a double belt press or kalander where consolidation takes place. Many GMT materials are produced in this way. It's also used for continuous reinforced plastics.

Clear advantage of the process is that no solvent has to be removed, as is the case in solution processing. Voids and surface problems are therefore avoided. Normal available granules can be used and the process is suitable for all thermoplastics.

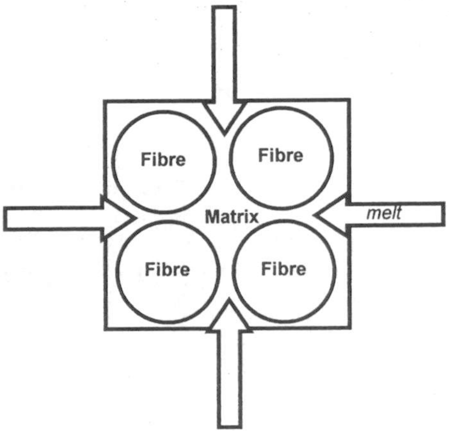


Figure 2.5: Melt impregnation

A problem is the high viscosity of the thermoplastic. The average viscosity of thermoplastics is 10^2-10^4 Pa s. Because many thermoplastics have decomposition temperatures that are only slightly higher than the melting point, viscosity can not be lowered sufficiently by raising the temperature. Even the thermoplastics with a relatively low viscosity (10^1-10^2 Pa s), like polyamides and polyesters, have difficulties entering the small interstices present between fibres (see figure 2.5). Another disadvantage is the large amount of energy needed to reach the high melt temperature of the plastics.

Film stacking

The film stack process makes use of thermoplastic films. Layers of these films are interleaved with the reinforcing fibres in the form of fabrics or mats (see figure 2.6). Impregnation is accomplished by using heat and pressure. The heat melts the film and the pressure forces it into the fibre material. Because a polymer melt is used in the actual impregnation step, the problems of this technique are the same as with melt impregnation.

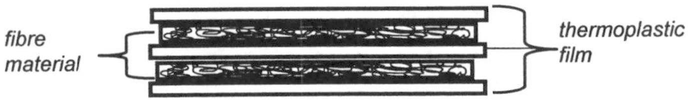


Figure 2.6: Film stacking

Impregnation can be done in a continuous process using a double belt press or discontinuous using an autoclave or hot plate press.

The advantage of this process is its flexibility. Many combinations of fibres and matrix are possible. Thermoplastic film is also widely available.

Disadvantages are the high investment costs, bad mix and low processing speeds.

Filmstacking is mainly used for producing composites with engineering plastic matrices for high tech applications in space and aerospace. It is also used in research on possible new composite structures.

Commingling

Commingling is the process in which matrix and reinforcement filaments or fibres are mingled into one tow [6,13]. This leads to a flexible preform that can be woven, braided or knitted into a fabric or used in a unidirectional form.

Coweaving is similar to this process. In coweaving matrix tows and reinforcement tows are woven together. The mixing in this process is not as good as with commingling. Fabrics from commingled yarns are sometimes processed into pre-consolidated laminates by calendering the fabric between rollers or a double belt press. Apart from good draping characteristics, flow distances for the molten polymer filaments or fibres are substantially reduced due to the intimate mixing (see figure 2.7). This is the reason why lower pressure and temperatures can be used in the final product pressing. Volume fractions can be precisely controlled and high fibre volumes can be achieved. Well developed textile processing techniques can used for commingled prepreg production.

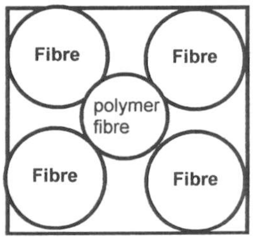


Figure 2.7: Commingling

A disadvantage of commingling is the difficulty of opening up the reinforcement fibre bundle to intermix the matrix fibres, especially because most reinforcement fibres are brittle.

Twintex, made by Vetrotex is a successful (thus cheap) commingled E- glass/PP yarn. It is available in roving, textiles, consolidated plates and pellets (www.twintex.com). Fibre volumes up to 75% by weight are possible.

Slurry processing

Slurry processing involves dispersing polymer powder in an aqueous suspension to form an aqueous slurry. This slurry is used to impregnate the fibre material. The water has low viscosity and is therefore a good medium for transporting the polymer particles into the fibres.

After impregnation, the prepreg is dried to remove the water. To prevent powder from falling off the fibers, normally the prepreg is exposed to heat to melt the powder onto the fibres.

Powder particles usually have a diameter between 5 and 50 micron. Slurries have to be stirred constantly to prevent these particles from precipitating.

An advantage of this method is that all polymers can be used. It is also clear that the use of water doesn't bring along the same environmental problems as in the case of solution impregnation.

A disadvantage is the fact that water has to be removed in a dry step. To obtain small powders, some thermoplastics have to be grained cryogenically, making them expensive.

To circumvent the problems of particle precipitating, dispersions can be used. Dispersions also consist of small polymer particles in water. The particles however are much smaller (less than one micron) than in slurries and they are made stable by the addition of a surfactant, so no stirring is required. These dispersions are the subject of chapter 3.

Dry powder processing

In this process, small dry polymer particles (20-200 micron) are deposited onto the fibre material (see figure 2.8). Several methods have been developed that differ in the way the particles are deposited on the fibers and the way the adhesion between the two is accomplished.

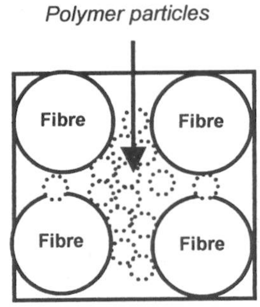


Figure 2.8: Commingling

In most processes electrostatic forces are used to create the adhesion: A fluidizing gas is charged by an electrostatic generator. This gas in turn charges the particles that start moving to the fibers that are oppositely charged. Instead of using a gas, low frequency vibration from acoustic energy can also be used to create a uniform dispersion. To prevent segregation of the particles after deposition, they are melted to the fibers. A tackifying agent or addition of a 'skin' around the powder-impregnated fibres can be used for the same purpose.

The process is suitable for all thermoplastics. If a small powder is used, a good impregnation can be achieved. The process requires no drying because no solvents are used. In comparison with the hot melt technique, heat exposure is short. Only the outside of the particle has to be melted to let it stick to the fibres. This reduces fibre and matrix degradation

The process has the same disadvantage as the slurry process: grinding thermoplastics is expensive.

2.5 The use of natural fibres in composite materials

advantages

Natural fibres like flax, jute and hemp offer good mechanical properties (see chapter 1).
These properties were also noticed by the composite industry, which started investigating the possibilities of natural fibres as an alternative for glass fibers in TPC's. These composites are called natural fibre reinforced plastics (NFRP's).
Table 2.2 lists the advantages that natural fibres can offer in these composites [5,17,20, 22]

***Property advantages*:**
- High specific stiffness
- Good thermal and acoustic insulating properties

Processing advantages
- Non abrasive
- Workers friendly

Environmental advantages:
- No net contribution to the CO2 in the atmosphere
- Thermal recyclable
- Renewable
- Low energy consumption

Economical advantages:
- Cheap
- Income for developing countries

Table 2.2: Advantages of natural fibres over glass

In table 2.3, some mechanical properties of flax and glass are presented. The values for flax fibres were taken as an average from the values in table 1.2. This table shows that both tensile strength and modulus for E-glass are higher. Owe to the low flax density however, the specific modulus for flax fibres is higher than for E-glass.

	flax	**E-glass**
Density [g.cm^{-3}]	1.51	2.54
Tensile strength [MPa]	626	3500
Specific strength [10^{6}m^2.s^{-2}]	0.42	1.38
Tensile modulus [GPa]	69.3	73.8
Specific tensile modulus [10^6 m^2.s^{-2}]	46	29

Table 2.3: specific properties of E-glass and flax

In composite structures that are designed on stiffness therefore, the use of these fibres can result in weight savings.

In a structure designed on strength, flax fibres are not a good alternative.

Natural fibres offer good thermal and acoustic properties which makes them suitable for noise shield in cars.

Natural fibres are less damaging for processing equipment compared to glass. This results in lower processing costs while moulds, extruders and other equipment can be written off over a longer period.

Flax is not as thin as glass, therefore reducing health problems like skin irritation and lung problems that occur in some processing techniques.

During disposal of flax fibres (by rotting or burning) the same amount of CO_2 is released to the environment as is needed to grow them. This neutral effect on the CO_2 balance is an important argument in a period where the greenhouse effect is of growing concern.

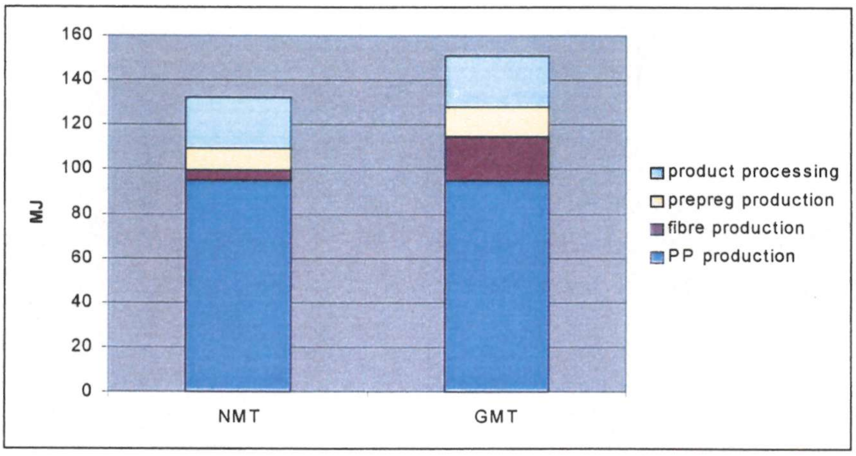


Figure 2.9: Energy distribution in the processing phase of NMT and GMT product (MJ/product)

If natural fibres are thermally recycled, there is no problem of glass residue that sticks to oven walls.

Natural fibres like flax, jute and hemp are quickly renewable. They can be harvested once (in some areas twice) every year.

The production of flax fibres requires much less energy than glass fibres.

Figure 2.9 shows a comparison between a flax-fibre reinforced polypropylene under floor panel (NMT) of a passenger car and a glass fibre reinforced panel (GMT) [7]. It shows that glass fibre production requires 5 times more energy. It also shows that most of the energy in the processing phase goes to the PP-production.

Natural fibres can be cheaper than glass fibres, although there are several dissenting opinions about this. For developing countries it's cheaper to use their own natural fibre production either than importing glass fibres with expensive currencies. In Europe however, it is uncertain if their own natural fibre products (flax/hemp) can compete with glass, especially when the subsidies on these products would disappear.

The use of natural fibres in composites could be a great new market for natural fibre producers in developing countries.

Disadvantages

In spite of all the advantages they offer, flax fibres didn't take over the strong position of glass in TPC's. Reason for this are several disadvantages flax fibres have in comparison to glass [5,17,20, 22] ,see table 2.4.

- Lower strength
- Restricted processing temperatures
- Variable quality and price
- Moisture absorption

Table 2.4: Disadvantages of flax fibres in TPC's

From table 2.4 it is clear that natural fibres have lower strength properties than glass, also when the specific strength is considered. Impact strength of NFRP's is also less and the main reason for the limited use of natural fibres in structural parts.

Natural fibres start losing strength around 220 °C. This strength loss is caused by hemicellulose degradation. This limits the choice for thermoplastics in NFRP's to those with low processing temperatures like PP, PE, ABS, PS, PMMA, SAN and PA 11. PP is the most popular thermoplast in NFRP's untill now. In GMT material, this plastic has a processing window of

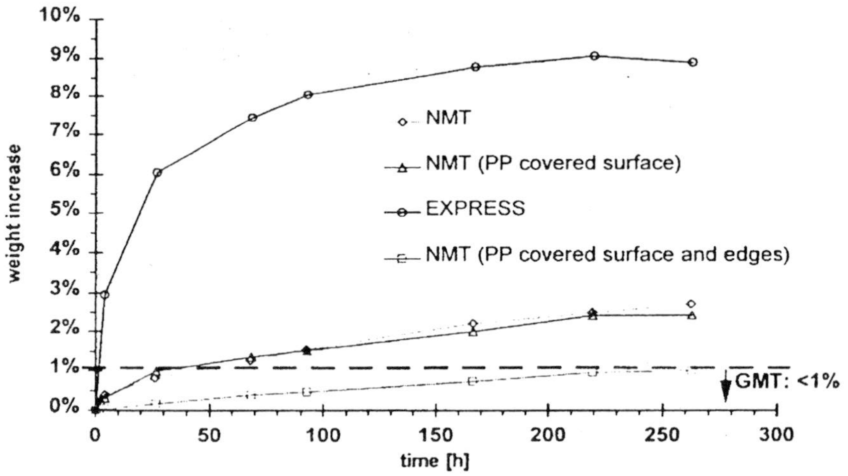


Figure 2.10 Water absorption of flax fibre reinforced PP

200 °C to 240°C with an optimum around 230°C. It is clear that NFRP's with PP has to be processed at the low end of this window. This limits the product complexity and sometimes makes the choice for a PP type with lower molecular weight necessary, which has a negative effect on composite properties.

Natural fibres are a product of nature and show large fluctuations in quality as already discussed in chapter 1. Price is also fluctuating like with many agricultural products. Price and quality uncertainty is an important reason for the reserved attitude industry has towards these fibres. The problems can be partly overcome by a better control over the production chain and fibre upgrading techniques as discussed in section 1.3.

Natural fibres are hydrophilic and absorb water. Moisture content varies between 5 and 10 %, and can lead to dimensional unstability and degradation of mechanical properties of the composite. Adjusting the compound materials and the processing makes it possible to reduce water absorption to a level similar to that of glass fibre composites (see figure 2.10). Even at these low moisture content however, mechanical properties can decline. Special fibre treatment, like in the Duralin process (see section 1.4) can reduce this decline.

2.6 Suitable NFRP prepreg processing techniques

There are many differences between glass and natural fibres as can be concluded from the previous chapters. Natural fibre characteristics will put constraints to the prepreg processing techniques discussed in section 2.4. These constraints will be indicated by discussing the following two aspects:

- Yarn structure
- Impregnation

Fibre structure

A natural fibre is built up of smaller individual fibres (see section 1.2). Natural fibre yarns are made by twisting several fibres into one yarn (spinning). This has the following effect on the choice of a suitable prepreg process:

1. Spinning is an expensive process. Fabrics made out of natural fibre yarns are in general more expensive than glass fibre fabrics [5]. Using these fabrics therefore doesn't seem to be the best way to produce a cost-effective material.

2. In many prepreg processes, continuous roving is spread before being exposed to the solution, melt, powder or slurry. In this way more fibre surface comes directly in contact with the matrix material. Because the twisted natural fibre yarns can't be spread, impregnation is more difficult. This means that higher temperature or pressure has to be

applied (melt) or smaller particles have to be used to let the matrix enter the yarns. (powder/slurry impregnation). It is clear that this makes the process more expensive and increases the danger of fibre degradation.

Impregnation

Cellulose, hemicellulose and lignin are the main constituents of a natural fibre. If these substances are heated, physical and chemical changes take place.

Physical properties include color, weight and strength; chemical changes include reduction of degree of polymerization and evolution of water. This can result in a decline of composite properties.

Chemical structure puts the following constraints to the prepreg techniques:

1. Processing temperature must be low
2. Processing time must be short

The problem remains that polymer viscosity of most polymers at temperatures around 200 °C is still high. Therefore more time is needed to impregnate the fibres than was the case at higher temperatures, which increases the chance of fibre degradation. It is clear that the optimum between time and temperature is very important in NFRP processing.

The use of a prepreg, in which fibres and matrix are well mixed, reduces the flow length for the matrix in the product-pressing step. Good consolidation can be achieved in less time and at lower temperature and pressure.

It is clear that using a melt is not the best way to make a prepreg: A high melt viscosity makes impregnation of yarns/mats difficult. It is also an extra heat exposure that can result in composite properties decline.

Because natural fibres can not be spread, dry powder is not able to impregnate the fibres well. The result will be that of a coating around the yarns. Impregnation of mats by dry powder has similar problems.

The fibre/matrix mix in a commingled yarn is good. The commingled yarns and woven are also easy to handle. The discontinuity of the fibre and high price of natural fibre woven will make it difficult to make this method cost-effective.

Because of the low solid content of thermoplastic solutions, solution impregnation has never been a popular process for thermoplastics. Environmental regulations on the use of solvents have been tightened, making the process even more unpopular. It also conflicts with the environmental friendly character of natural fibres. Furthermore solvents can have a negative influence on natural fibre properties, although no research has been done to determine this.

Slurry processing seems to be a good method for NFRP prepregging. There is minimum heat exposure (only a short heating cycle to melt the particles to the fibres) and therefore fibre damage is avoided. The low viscosity of water helps to transport the small particles into the fibre structures. A special kind of slurry, called latex, will be discussed in chapter 3.

2.7 Current applications and processing techniques of plant fiber composites

As said before, natural fibre reinforced thermoplastics have entered the market for interior parts of cars and trucks in recent years. Typical applications are trim parts and door panels (see figure 2.13) The share of natural TPC's however is much less than that for natural fibres reinforced thermosets, as can be seen in figure 2.11. The fibres in most of these composites are small and replace fillers like talcum,calcium and glass.

Source:A.Maqurno (1999)

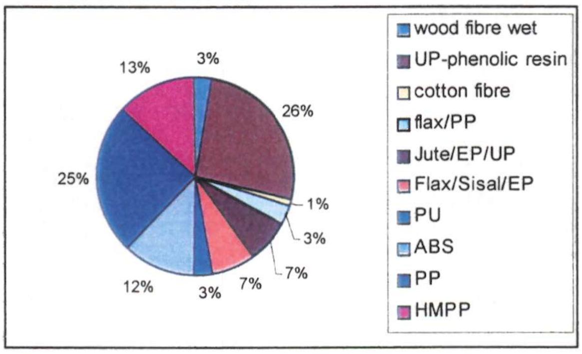


Figure 2.11: Market share of trim panel materials in W.Europe (1997)

The main processing techniques for natural fibre reinforced thermoplastics are:

1. **Compression molding**
    - Commingled mats/ woven
    - NMT
    - EXPRESS
2. **Injection molding**

ad 1) Compression molding is a technique in which TPC prepreg is heated and subsequently pressed into a mould. Several compression molding techniques have been developed that all differ in the way the forming pressure is applied: matched tool molding, rubber-die molding , diaphragm forming and hydroforming. Compression molding is suitable for long fibre composites. There are several companies that make NFRP prepreg suitable for this process. Schillgen (Germany) delivers commingled woven of PP and flax. Johnson Controls automotive (Italy) delivers LoPreFin™ and Fibroflax™, Flax/PP and Sisal/PP mats made by mixing natural and PP fibres in a closed mixing chambre until a homogeneous mixture is obtained [17]. This same company also makes a TPC's of wood and PP by mixing 50% wood flour and 50% PP that is extruded in a sheet that can be compression molded.

The extrusion press process (EXPRESS) doesn't use a prepreg (see figure 2.12). In this process, PP is extruded on the fibre mat in the mould, just before pressing. This method is used by Daimler Benz. [31].

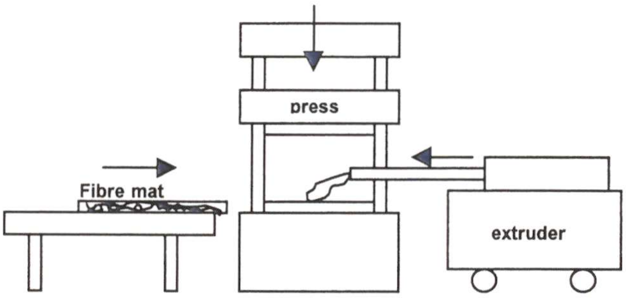


Figure 2.12: EXPRESS process

ad 2) Injection molding is used for thermoplastics with small particles natural fibres. The two materials are mixed in an extruder and injected in a closed mould. An example is COIXIL™ (Johnsons Control automotive), a sandwich material with a TPO skin and a core material of short fibre reinforced polyolefin.

NFRP's didn't enter other markets than the automotive applications on the same scale. NFRP's however have the possibilities to enter markets like consumer goods and furniture. Typical applications could be computer housings, seat shells, etc.

Figure 2.13: NFRP indoor panel

3. Polymer dispersions

The use of polymer dispersions in processing NFRP's could be a way to overcome impregnation problems due to the high polymer melt viscosity. This chapter discusses the different aspects of polymer dispersions. Section one is an introduction to the subject. It gives a definition of a dispersion and discusses the important expressions involved. The chemical structure of dispersions is discussed in section 3.2. Most emulsions are made by the emulsion polymerization process (section 3.3) Section 3.4 gives the most important polymer dispersions and their applications. An overview of latices that could be used in NFRP's is given in 3.5.

3.1 Introduction into polymer dispersions (latices)

A dispersion can be defined as a stable mixture of finely divided (dispersed) solid particles in a continuous fluid [2, 26] The word colloid is an often used synonym. Water is often used as the fluid in dispersion, however other fluids can also be used as the continuous phase (not included in this discussion). When the dispersed phase in the fluid is also a fluid, it is called an emulsion. A good example is milk, in which fat droplets are dispersed in water (stabilized by protein).

It is difficult to give a good definition of polymer dispersions. This is because the large variation in polymer behavior, depending on glass temperature, chain length, molecular mass, etc.

Polymers with low chain length are low viscous fluids, at high length they can be hard solids. Below the glass transition temperature they have a glassy character, above this temperature they are viscous. This character between fluid and solid is the reason why polymer dispersion are sometimes also referred to as polymer emulsions, although at normal ambient temperatures, most industrial polymers more closely resemble solids than liquids. Another reason why polymer dispersions are often referred to as emulsions is the fact that some synthetic polymers are produced by a chemical process called emulsion polymerization (see section 3.3).

'Latex' refers to the milky appearing sap of certain plants such as milkweed, lettuce and rubber trees. In fact they are colloids of natural rubbers suspended in water. Synthetic substitutions of these natural rubbers, Butadiene-Styrene-Copolymer dispersions, are also called 'synthetic latexes' or simply latexes/latices. Nowadays the word latex is used for stable colloidal dispersions of a polymeric substance in an aqueous medium.

The words latex, polymer emulsion, polymer dispersion and polymer colloids are used interchangeably when talking about polymer dispersions, which makes it sometimes a little confusing.

Since the development of the first synthetic polymers around 1920, there has been a tremendous growth in the use of these materials. The prediction for this year is that more than

190 million tons will be produced [26]. The most important polymers are polyolefins (PP/PE), PVC and PS. Together they comprise 68% of the total synthetic polymers production. The group of dispersions form 7% of the total synthetic polymer production. In this number the emulsions used as impact modifiers for plastics (2 million tons a year) are excluded, because they are not sold on the market but used directly by the polymer manufacturers.

More than 10 million tons of dispersions are produced every year for many different applications. The use of latices as paint is a good example. Latices are however also used as filmformers in printing inks, adhesives, paper varnishes, carpet backing, etc. Besides they are used to enhance material properties. In this respect the use of latex in cement to improve flexibility and thermal expansion properties is a good example.

3.2 Structure of a latex

As already mentioned in section 3.1, a latex consists of evenly distributed fine polymer particles in water. Typical particle diameters are 50-500 nm [2] Industrial dispersions have a solid content between 40 and 60 per cent. This is in fact a thermodynamically unstable situation. Synthetic polymers are hydrophobic and want to agglomerate to decrease the surface exposed to the water. In this way large particles will be formed and finally a total separation of polymer and water takes place.

Agglomeration can be avoided by giving the particles an electric charge. The electric charge causes the particles to repel each other, resulting in a stable latex. According to the polarity of the electric charge, which is present at the surface of the particle, latices can be classified into three groups:

- *Anionic latices*; the particles carry negative charges at their surfaces.
- *Cationic latices*; the particles carry positive charges at their surfaces.
- *Non-ionic-latices*; the particles are uncharged electrically, stabilization takes place by attaching hydrophilic groups to the particle surface.

The anionic and cationic latices together form the group of ionic latices. The ionic–active species (surfactants) can be attached to the particle by adsorption or by a covalent bond at the particle-water interface. A combination of these two is also possible.

Although during processing (and shelf life) a stable latex is required, in almost all the applications the polymer particles have to agglomerate to form a stable film (for example in latex paint). This can be done by removing the water by drying, freezing of the water, mechanical agitation or by adding certain chemical agents (salts, acids).

Most of the industrial latices are anionic. Cationic latices are found in some special applications. Till now, non-ionic latices find no significant industrial application.

3.3 The emulsion polymerization process

In general, there are two ways to make latex [2]

- By dispersing a polymer (solution) in water under high shear conditions ("artificial latices")
- By polymerization of monomer molecules, mostly starting from monomer-swollen micelles ("emulsion polymerization").

In the first case, a polymer has to be dissolved into a diluent. Most of the synthetic polymers (like PP, PE) are of high molecular weight and are thus very viscous. It is difficult to shear bulk material or even solutions of these polymers into smaller particles. There are only few examples of latices made this way, but it takes large amounts of mechanical energy and emulsifying agents to make them. This makes the process very expensive and therefore only attractive for some specialty products.

In the second case, the polymer particles are formed by polymerization of smaller (monomer) molecules. This process is called emulsion polymerization. More than 90 % of the latices are made by this process.

The process uses the following basic ingredients:

- Surfactant
- Monomers
- Water
- Initiator

A surfactant is a molecule with two moieties of different solubility. One end, termed the tail, is soluble in nonpolar, organic compounds. The other end, the head, is polar and water soluble see figure 3.1.

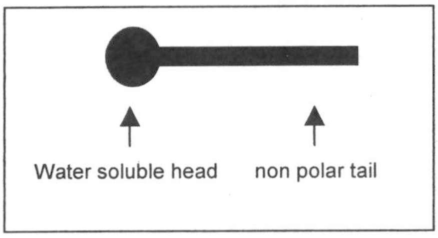


Figure 3.1: Structure of a surfactant

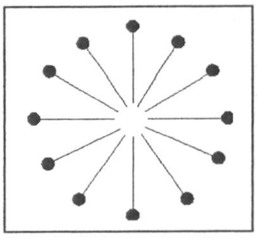


Figure 3.2: Structure of a micelle

When a certain surfactant concentration (the critical micelle concentration (CMC) in water is reached, the surfactant molecules aggregate into a 3-D structure, with their non-polar tails directed towards the centre of the structure and the water soluble heads pointing to the outside. This structure is called a micelle (see figure 3.2). The interior of the micelle provides the site necessary for polymerization.

When the micelles are formed, monomer and an initiator are added. Because of the hydrophobic character of most monomers, the gather in the hydrophobic centre of the micelles and in large –size droplets with surfactant molecules on the outside. The polymerization of these monomers starts when the initiator starts forming free radicals. A radical migrates into a micelle and reacts with a monomer molecule. The newly formed radical reacts with another monomer thereby forming a polymer. Once polymerization starts, the micelle is referred to as a latex particle. Monomer migrates from the large monomer droplets via the aqueous phase to the micelles to sustain polymerization. The polymerization process stops if all monomers are used.

Emulsion polymerization is a simple process that can produce high molecular weight polymers at high reaction rates.

3.4 Important latices and their applications

Monomers are the building blocks for polymers. The choice for a certain monomer depends on criteria like the polymer end-use: the compatibility with possible pigments and fillers and the processability. Monomers have the most dominant effect on the end-use characteristics. Table 3.1 lists the most important monomers.

In many cases, the desired properties can not be achieved by using only one monomer. Therefore, frequently copolymers of glassy and rubbery polymers are used.

End-use characteristics not only depend on the choice for the bulk monomer. Many functional monomers (normally between 1-3 %) can be copolymerized with the bulk monomers. They provide reactive sites for crosslinking, surface modification or adhesion.

monomer
Butadiene
Styrene
Acrylonitrile
Ethylene
Vinyl chloride
Vinyl acetate
Vinylidene chloride
Acrylates
methacrylates

Table 3.1: Important monomers

Because of the large variety of bulk and functional monomers, suitable latices can be made for many applications [3]. Figure 3.3 shows the most important synthetic latices and their share in the total market.

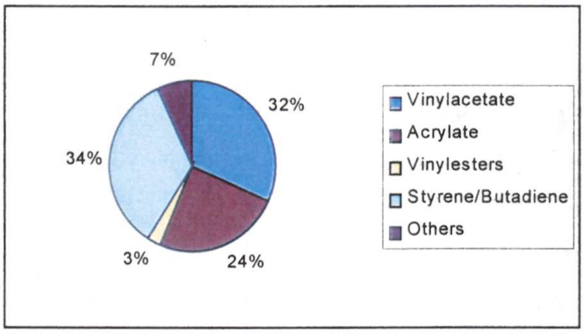


Figure 3.3: Market share of important monomers/polymers used in latices

Typical applications for these latices are:

- *Polyvinylacetate and* copolymers:
  paper coatings, paints and adhesives;
- *Styrene-Butadiene copolymers*:
  carpet backing, paper coating, paints and non woven binders;
- *Butadiene- Styrene copolymers and polybutadiene:*
  synthetic rubbers
- *Polyacrylate copolymers:*
  paints and non woven binders.

Figure 3.3 excludes the latices of the commodity polymers ABS, HIPS and PVC latices. These latices are a necessary product in the processing chain of these plastics. The polymer particles in these latices are coagulated by adding a salt or acid. The coagulum is then filtered and dried. The remaining dry polymer particles can be processed into granules that are the feedstock for the plastic processing industry. These latices are hardly used directly in typical latex applications, mainly because their film formation temperature is too high (see section 4.2).

3.5 Use of latices in NFRP processing

As discussed in chapter 2, the use of latices could be a good alternative to other prepreg processing techniques. This will be explained by discussing the following aspects:

- *Viscosity aspects*

- *Surface free energy and wetting behavior*
- *Drying of the deposits*
- *Environmental and safety aspects*
- *Costs aspects*

Viscosity aspects

High melt viscosity is one of the main problems in processing TPC prepregs. Depending on shear rate and pressure, values for polymer melt viscosity at processing temperature vary between 100-10.000 Pa.s.

One way to reduce the viscosity is the use of a solvent. In a solution, polymer molecules are extended and molecularly dispersed. Because of the extension, polymer molecules seriously interfere with the flow behavior of the solvent. The solution viscosity therefore increases rapidly if more polymer is added to the solvent (see figure 3.4) Even at low polymer content (5-10%) polymer solutions are jelly like. A 20% polymer content is a practical limit for these solutions.

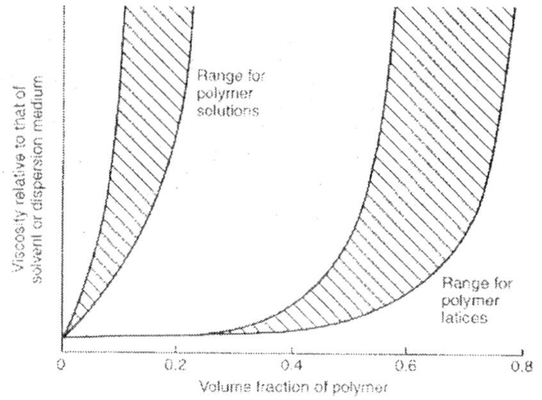


Figure 3.4: Viscosity as a function of volume fraction

The polymer molecules in latex are tightly aggregated into particles. Because of their hydrophobic character, they will have little tendency to interact with the water.

Polymer content has less influence on the flow behavior of the latex. As can be seen from figure 3.4 the viscosity of a latex is constant until the volume fraction reaches a value of 40 % by weight. At this point the polymer particles start to hinder the flow of the water. At a further increase, the particles come so close together that the flow of water is seriously restricted and a sharp rise in viscosity can be observed.

Typical values for a 35% volume content latex is 0,015- 0,05 Pa.s. This is around 200.000 times lower than for the polymer melts.

Surface free energy and wetting behavior

To obtain a good wet out of fibres by a matrix material, the surface free energy of the solid (fibre) must be higher than that of the matrix, and polarity of the two materials must be in the same range (γ_{sl} must be low). (See chapter 6 for an explanation of surface free energy and wet out).

The high polarity of natural fibres normally makes a good wet out by a highly a -polar polymer melt or solution difficult. The surface free energy of latices is much higher than for polymer solutions or melts. This makes a wet out of polar (greasy) surfaces more difficult. The wet-out of polar surfaces like wood and natural fibres however, is improved because latex has similar polarity (and solid/liquid interfacial energy is therefore low) [2]. The use of latices could therefore reduce wet-out problems in NFRP prepreg processing.

Drying of the deposits

If drying out of deposits is concerned, latices are at a disadvantage. Organic solvents are more volatile, mainly because of lower heats of vaporization. The heat of vaporization for water is 2.257 kJ/g and rather high compared to the value of 0.356kJ/g for cyclohexane, a typical solvent for hydrophobic polymers. If the lower polymer content of solution is considered, the overall situation is a little better.

From an energy point of view, latices are also at a disadvantage compared to composite processing techniques that use polymer melts. Figure 3.5 shows a comparison between the latex and melt prepreg processing techniques. In case 1, 1 kg of flax fibres is impregnated by ABS latex with a solid content of 50% by weight. After impregnation, the flax has to be dried. This means that the temperature of both flax and polymer particles has to be raised to the drying temperature (100 °C). In case 2, 1 kg of ABS granules is melted at 200 °C and added to the flax fibres.

Assumptions	
Polymer Type	ABS
ABS latex solid content	50 % by weight
Water vaporization heat	2.257 kJ/g
ABS melt enthalpie at 200 °C	220 J/g
ABS enthalpie at 100 °C	115 J/g
Specific heat flax fibres	2.5 J/g K
Case 1: impregnation of 1 kg fibres by 2 kg of latex	
Water vaporization energy	1000*2.257 10^3 = 2.257 *10^6 J
Enthalpie raise ABS particles	1000* 115 = 1.15*10^5 J
Enthalpie raise fibres	1000*2.5 *80 = 2 *10^5
Total	2.572* 10^6 J
Case 2 : impregnation of 1 kg fibres by 1 kg polymer ABS polymer melt	
Enthalpie raise PS	1000* 220 = 2.2*10^5 J

Figure 3.5: Energy comparison of melt and latex impregnation

From this example it can be concluded the processing of a fibre mat by latex roughly requires 10 times more energy. Two aspects however, need to be considered:

1. Latices produced by the emulsion polymerization process require drying to obtain granules. Although this is mainly done by mechanical drying (spin dryer), part of the water also has to be evaporated.
2. Part of the vaporization energy can be regained.

Environmental and safety aspects

Latices have many technological and environmental advantages over polymer solutions. Solvents normally are expensive and recovery of the solvents is very costly. Many solvents are toxic or flammable, making them hazardous to use on an industrial scale. Water is a safe and environmentally friendly product.

There are no expensive recovery installations needed. The use of latex contributes to the environmental friendly character of NFRP's.

Costs aspects

As explained in section 3.3 in general there are two ways to make latex. The preparation of "artificial" latices is very expensive. It is only used for specialty products and can never be a cost-effective way to make NFRP's. The use of a PP or PE latex therefore can never be an alternative to processes that use polymer melts. The only reasonable way to make cheap bulk latices is the emulsion polymerization process. There is no extra process step necessary to make these latices, moreover a plastic producer can omit a process step: drying. Because drying represent a large part of the final plastic costs, the price for these latices will be much less than the plastic granule price.

The costs for transportation of the plastic (granules or latex) have a considerable impact on their final price. Here the latices are in a clear disadvantage. Normal latices have a solid content between 30-45 %. This means that more than half of the weight transported is useless (water). Manufactures are therefore constantly trying to increase the solid content. In ABS a solid content between 50-60 % is already possible. At those levels there is a sharp increase in latex viscosity, so the content can not be increased endlessly.

There are a few latex characteristics that could save costs in the processing of NFRP's:

- The use of an expensive solvent is omitted
- The processing temperatures are much lower than in melt processing
- A low viscosity reduces the costs for pumping and mixing equipment

3.6 Suitable latices for NFRP's

In section 3.2 several applications for latices were discussed. Although latices are used as a binder in non-wovens, there is no information about latices being used as matrix material in fibre reinforced plastics. Most of the latices on the market today therefore will not satisfy all the requirements for a matrix in TPC's.

Latex paint for example is cheap, safe, storable and easy to process and apply. Compatibility of these paints with cellulose containing materials like wood and paper is excellent. Strength, flexibility and strain however are low, and therefore they can not be used in NFRP's.

In section 3.4 the wide variety of monomers and possible functional groups are discussed. Innumerable combinations between these two are possible with a large variety in latex properties. It can therefore be expected that latices can be 'designed' that are useful as matrix material in TPC's. Designing of latices is a costly activity that takes time. To explore the possibilities of prepreg processing with latices, therefore existing latices have been used. PVC, ,SAN, ABS, HIPS and PMMA latices are interesting in this respect. As already mentioned in section 3.3 these latices are not sold on the market as a latex, but are a necessary step in the processing of plastic granules. Some properties of these plastics are given in table 3.2.

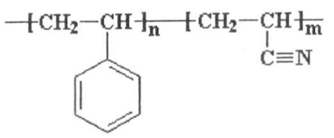
Source: literature (29) and www.matweb.com

Polymer	Density [g/cm^3]	Tensile strength [MPa]	Tensile modulus [MPa]	Strain [%]	Notch strength [KJ/m^2]	Processing temperature [°C]
ABS	1.05	20-50	1600-3000	15-30	8-30	204-260
SAN	1.08	70-80	3600	5	3	240-250
PVC	1.38	50-80	2900-3400	20-40	2-5	199-210
PMMA	1.18	50-80	3300	3-7	2-3	243-250
HIPS	1.05	20-50	1600-2500	20-50	5-10	216-246

Table 3.2: Mechanical properties of important thermoplastics

SAN (styrene-co-acrylonitrile) is a simple random copolymer of styrene and acrylonitrile (see figure 3.6). It is an amorphous polymer with a glass transition point at 105 °C. As can be seen from table 3.2 it is a strong and stiff polymer. Impact strength however is low.

Applications for SAN include dishwater-safe containers, oil resistant containers, packaging for foodstuff and cosmetics. SAN has good resistance to weathering and can thus be used for outdoor applications.



SAN

Figure 3.6: SAN molecule

Processing temperatures for SAN are far above the temperature at which vegetable fibres start degrading (see section 2.5), what makes SAN unsuitable for NFRP's.

ABS (acrylonitrile-co-butadiene-co—styrene) has better impact toughness than SAN. It's made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Polybutadiene has carbon-carbon double bonds in it, which can polymerize with styrene and acrylonitrile, leading to SAN grafts. So ABS consists of a polybutadiene chain with SAN chains grafted onto it, as can be seen in figure 3.7. By addition of polybutadiene in ABS, a polymer can be designed with desired properties: a high content improves impact toughness but reduces stiffness, a low content has the opposite effect. Applications for ABS include vacuum cleaner covers, lawn mower housings, telephone handsets, drain pipes, golf carts. It also has many applications in the automotive industry.

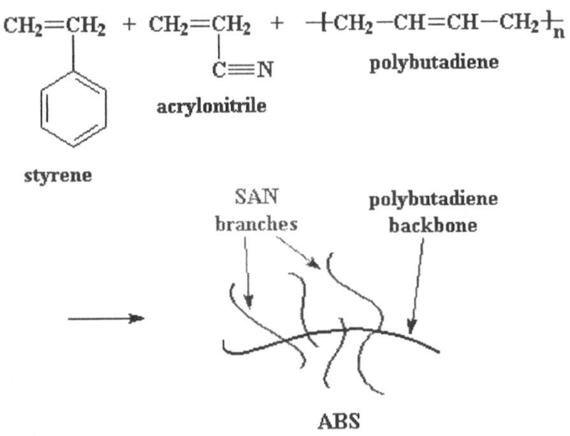


Figure 3.7: ABS molecule

The addition of polybutadiene to SAN has a lowering effect on processing temperatures. There are certain ABS grades that can be processed below 220 °C and can therefore be used in NFRP's. The use of ABS in these composites could enhance the bad impact characteristics of NFRP's.

PVC (Polyvinyl Chloride) is produced by polymerization of vinyl chloride, see figure 3.8. Although this monomer is suspected to cause cancer, nowadays PVC is free from monomeric vinyl and not considered a potential carcinogen anymore.

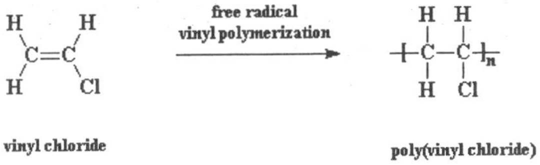


Figure 3.8: PVC molecule

There are two types of PVC: plasticized and rigid PVC.

Plasticized PVC is flexible, and usually rubbery at room temperature. Typical applications are domestic electric cable, garden hoses and automotive door seals.

Rigid PVC has high density compared to the other plastics in (table 3.2), and is very brittle. It has a high melt viscosity and due to thermal unstability, viscosity can not be reduced by increasing processing temperatures. Advantage of PVC are its flame retardancy and low price (like PP and PE). Typical applications include pipe, rainwater goods, window frames and bottles. PVC film is used for packaging of several goods.

Processing temperatures of PVC are below those for vegetable fibres. The flame-retardant characteristic of PVC could reduce the problems of the flammable vegetable fibres.

Because PVC has a low impact strength, it is not the best choice to improve impact properties of NFRP's.

PMMA (Polymethyl methacrylate), see figure 3.9, is an amorphous polymer better known as Plexiglass. It has the highest light transmittance of any plastic material, which is the most important reason for the use of the plastic. It also has a very low sensitivity to UV light and oxidation and an overall high weather resistance. PMMA is brittle and scratched easily. There are also impact grades available with enhanced toughness.

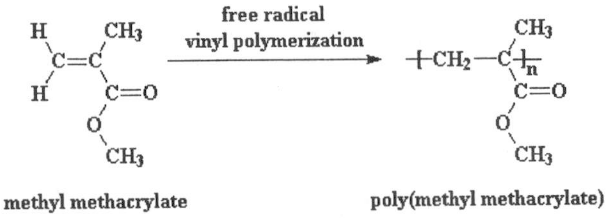


Figure 3.9: PMMA molecule

Because of its clarity PMMA is used for windshields, skylights, automobile lights, compact discs and outdoor signs.

Because of the high processing temperature, high brittleness and low impact toughness, PMMA doesn't seem to be a good option in NFRP's

HIPS (High impact polystyrene) is a copolymer of styrene and polybutadiene (see figure 3.10). The polybutadiene chains reduce the brittleness of ordinary PS and improve impact toughness. HIPS is used in many application were impact toughness is required.
Applications are toys, games and sports equipment, electrical equipment housings and refrigerator liners and fittings.

The mechanical properties for HIPS are similar to those of ABS. Processing temperatures are however close to the limit for NFRP's. The impact toughness is somewhat lower than for ABS.

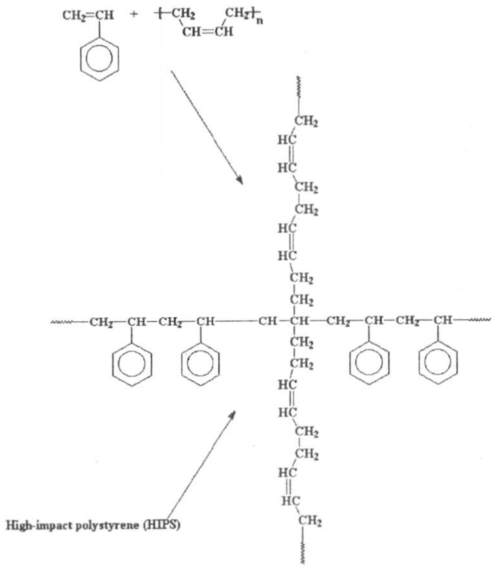


Figure 3.10: HIPS molecule

3.7 Conclusions

- Latex is a stable mixture of finely divided small (50-500nm) polymer particles in water, made by the emulsion polymerization process.
- Typical applications for latices are paper coatings, paint, carpet backings and non woven binders. Latex is not used as matrix material in composites till now.
- The use of latex in prepreg processing techniques good be a good alternative to known techniques because of the low viscosity, polar nature and environmental, safety and cost advantages.
- The latex prepreg process uses much more energy than a melt prepreg process.
- ABS, HIPS and PVC are interesting latices for NFRP's because of the relative low processing temperature and good mechanical properties. They are however hard to obtain because of their limited use in typical latex application areas.
- Suitable latices for use in composites must be 'designed'. Research in this area is required but is expensive.

4. Materials and processing aspects of latex prepregs

In the framework of this thesis, latex prepreg was made and tested. Section 4.1 discusses the materials that were used. The process aspects of latex prepregging are discussed in section 4.2. Aspects that are included are mat preparation, impregnation, drying and prepreg pressing.

4.1 Materials

Latex characteristics

Most of the dispersions that could be used as a matrix in latex prepreg (see section 3.6) are not directly available on the market. Polymer producers are careful in providing these latices, mainly because they don't want the chemical structure of their product to become public.

Finally two different latices were obtained:

BASF kindly provided Acronal 12 DE. Acronal 12DE is an acrylonitrile acrylic copolymer, normally used as a component for adhesives. Important product data is given in table 4.1. Mechanical data was not given by the producer and therefore acquired by testing.

The second product was ABS latex, kindly provided by DSM in Geleen. The ABS copolymer in this latex contains 40% polybutadiene and 60% SAN. Normally, SAN is added to this latex to reduce polybutadiene content. This improves the modulus of the latex. Unfortunately pure SAN could not be obtained within the timeframe of this research. This is the reason why the mechanical properties for the ABS latex, given in table 4.2, are lower than for ordinary ABS (see table 3.2). The data in table 4.2 is also acquired by testing.

Product	Acronal 12 DE
Solid content latex	39.8%
Mean particle size	0.1µm
Film forming temperature	50 °C
Viscosity latex (at 23 °C)	14-38 mPa s
Flexural modulus	3.1 Gpa
Flexural strength	90.2 MPa
Melt temperature	190 °C

Table 4.1: Acronal 12DE properties

Product	ABS
solid content latex	26.7%
Mean particle size latex	0.2 µm
film forming temperature	90 °C
Flexural modulus	1.04 GPa
Flexural strength	33.4MPa
Melt temperature	160 °C

table 4.2:ABS properties

Fibre characteristics

The natural fibres used in the research were dew retted flax fibres in the form of a mat delivered by Ceres BV. In this mat, fibres with lengths between 1 and 3 cm are more or less randomly oriented (see figure 4.1). On specific places, the fibres are punched together with needles to obtain a more or less stable 3D structure. During mat processing, the fibres are slightly orientated, resulting in anisotropic properties: in longitudinal direction strength and stiffness are less than in transverse direction.

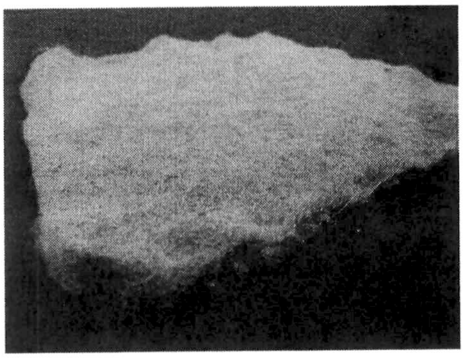


Figure 4.1: needle punched flax mat

In general strength and stiffness of mats are less than those of fabrics and continuous fibres. The reason for this is the randomness of the fibres: in a uniaxial loading, only a small fraction of the fibres carry the full load.

The reasons for choosing flax are the fact that flax fibres show good properties compared to jute and hemp (see chapter 1), and availability. At the moment it is hard to find random jute or hemp mats. The mat structure was chosen because it is the only fibre structure that has potential to compete with glass fibres (see chapter 2).

4.2 Processing aspects

The processing of the NFRP material will be discussed by treating the following aspects:

- Mat preparation
- Impregnation
- Drying
- Pressing

Mat preparation

The fibre mats were cut in the desired shape using scissors. The outer parts of the mats clearly had lower fibre density. This can have a large influence on NFRP performance. Therefore these parts were left out. The mechanical properties in transverse and longitudinal direction were found to be unequal. This will have an effect on final NFRP properties. Therefore a felt–tip was used to indicate the longitudinal direction.

Natural fibres always contain a certain amount of water. A quick test showed this amount was around 10% on fibre weight. Although water content depends on relative humidity, this amount was used as a standard. Fibre weight was determined by weighing the 'wet' fibres and subtract 10% (see appendix F)

Impregnation

Two different methods have been tried for applying the latex to the fibre mat:

1. Applying the latex using a paint roller; This is a clean method and offers a good control over deposited latex weight.

2. ‘Washing’ and squeezing; The mat absorbs latex around 13 times the fibre weight. Because only a weight gain between 5-8 times is desired, the remainder has to be removed by squeezing.

The following results were obtained:

- Using method 1 didn’t result in an evenly impregnated mat. A microscopic photo of the cross-section of the mat (figure 4.2) shows that most polymer particles are situated on the outer surface. There is almost no penetration of the particles to the inside.
- It took more than 45 minutes for the mat to get soaking wet by latex without additional pressure. The mats were ‘washed’ to speed up the process. A microscopic photo of the mat cross-section (figure 4.3) shows that method 2 gives a good and even mat impregnation.
- The structure of the mat is weak. The mat is drawn out during squeezing (method 2). This can have a negative effect on final composite properties.

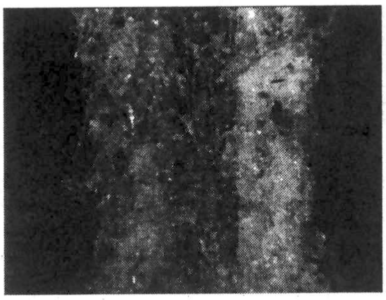


Figure 4.2: Paint roller impregnation

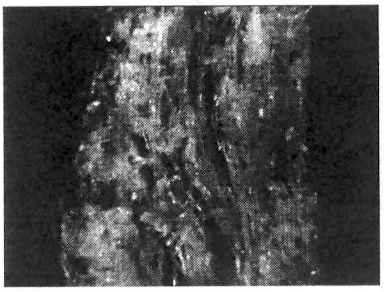


Figure 4.3: Washing and squeezing

If a dispersion flows through a porous medium, the solid particles can be separated by several filtration/ separation mechanisms [18]. This phenomenon can also appear if latex is flowing through a mat structure (see figure 4.4). Because latex particles are captured in the structure, the solid content of the outgoing latex flow is lower than that of the entering flow. In a continuous process, in which many meters of mat are transported through a latex bath, the non-constant solid content of the bath makes it difficult to control latex particle content of the final prepreg material.

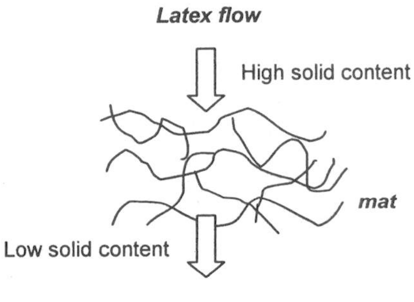


Figure 4.4: Filtration of latex

A test was done to determine the separation effect of the flax mat on ABS latex. Five circles were cut from the mat, dryed (90 °C, 45 minutes), weighed, and stacked in a cylinder with the same diameter as the mat pieces (see figure 4.5). ABS latex was poured on top of this stack. After 45 minutes, the superfluous latex was poured from the cylinder. The mat pieces were taken out of the cylinder and weighed. Then they were dried for 45 minutes on 90°C and weighed again. The results of the measurements are given in table 4.3.

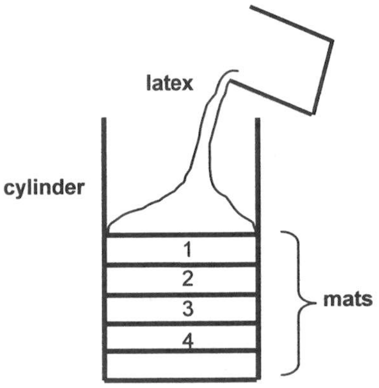


Figure 4.5: test set-up for filter effect

Mat nr.	A: dry weight [g]	B: weight after impregnation [g]	B/A	weight after drying [g]	latex solid content in mats [%]
1	1.55	19.43	12.53	5.91	0.24
2	1.20	14.94	12.46	4.27	0.22
3	1.31	16.02	12.23	4.59	0.22
4	1.44	17.22	11.96	5.00	0.23

Table 4.3: filtering effect of flax mat on ABS latex

The following conclusions can be drawn from this table:

- The B/A ratio decreases from mat nr.1 towards nr.4. Apparently the impregnation time was too short for the inner mats to get fully soaked.
- The difference in latex solid content between the mats is small. Apparently the latex particles can flow freely throw the mats and there is no separation. The solid content in all mats is lower than that from the pure latex (26.7 %). This could be explained by filtration of the larger particles at the upper surface of the first mat. The solid content of the latex in the first mat is not higher than for the pure latex (as would be expected in this theory) because the large particles are removed from the mat during removal of the excessive latex from the cylinder. The differences in solid content are too small however to draw firm conclusions.

Prepreg drying

Drying conditions have a large influence on final properties of latices, which will be clarified by discussing the following aspects:

- Film formation
- Migration

Film formation; Three phases can be distinguished in the drying process of latices (see figure 4.6). In the first phase (I) the latex particles are in Brownian motion. The rate of loss of water in this stage is constant and similar to that of pure water. In the second state (II), the particles begin to come into close contact with each other. This normally happens at a volume fraction of 0.6-0.75.The rate of evaporation decreases because the area of interface between the aqueous phase and air decreases. In the final stage (III), the rate of evaporation is low. The remaining water is lost by diffusion. The final appearance of the dried latex is that of a layer of dried latex powder or of a coherent film (see figure 4.7). Film formation is preferred in almost all latex applications.

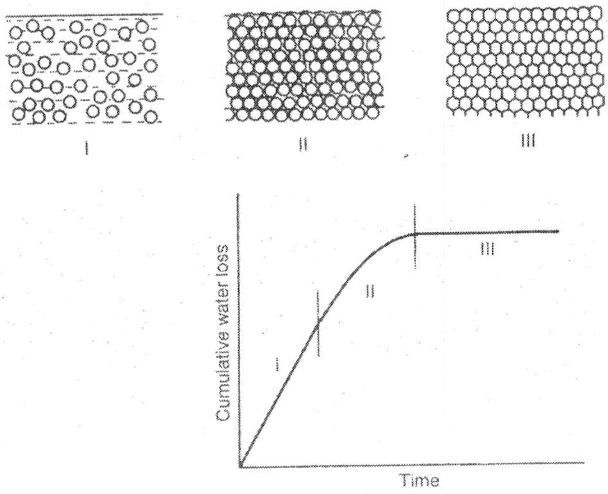


Figure 4.6: Drying process of latices

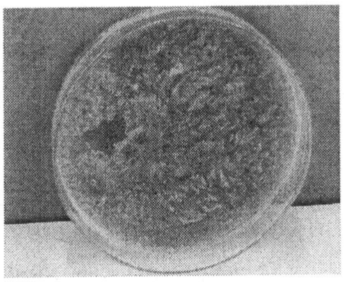


Figure 4.7: Film formation in Acronal

There are several theories that explain the interparticle coalescence [ ]. According to Brown's theory, there are two main driving forces:

1. Surface tension forces (F_{st})
2. Capillary forces (F_{cf})

Ad 1) When two particles coalesce, the surface area is reduced. This causes a reduction in surface free energy. According to Frenkel, the tendency to flow together can be expressed by the following equation:

$$\theta^2 = \frac{3\gamma t}{2\pi\eta a} \qquad \text{(eq. 4.1)}$$

In which (see figure 4.8):

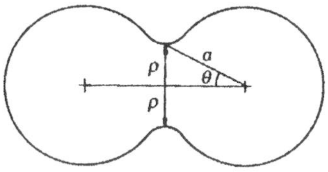


Figure 4.8: Particle coalescence

Θ = Half-angle of coalescence in radians
γ = Surface free energy of the polymer particle
η = Viscosity of the polymer
a = radius of the particles
t = time of coalescence

From this equation it is clear that particle coalescence increases with increasing surface free energy and decreasing radius and viscosity.

Ad 2) If water evaporates from the latex, menisci appear between water and air (see figure 4.9). The forces that result from this are called capillary forces, and will move the meniscus toward the air between the particles. The particles in turn will move towards eachother. If the polymer particles are small, like in latex, the formation of menisci can lead to considerable pressures.

A third force between particles is caused by the v.d. Waals forces (Fvdw). These forces are much smaller than the other two.

According to Brown, the following two forces resist the formation of a film:

3. Deformation resistance (F_w)
4. Coulomb forces (F_c)

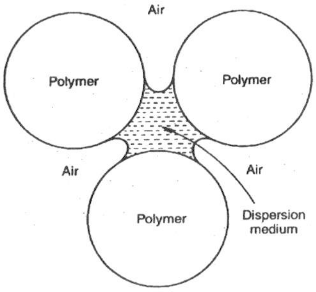


Figure 4.9: Formation of menisci

Ad 3) Every solid substance offers deformation resistance. Resistance decreases for thermoplastics when temperature is raised. Around 10 °C below the glass transition temperature (Tg), deformation resistance is low enough to form a continuous film. The temperature at this point is called minimum film formation temperature (MFFT).

Ad 4) Most latices are stabilized by surfactants that carry an electrical charge. This causes the different latex particles to repel eachother (see section 3.3). The force that is responsible for this repulsion is the Coulomb force, and is formulated by the following equation:

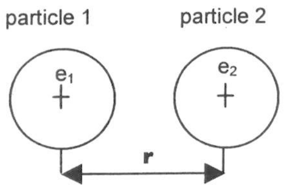


Figure 4.10: Coulomb forces

$$F_c = \frac{K * e_1 * e_2}{r^2} \qquad \text{(equation 4.2)}$$

In which:

K = a constant
e_1 = electrical charge particle 1
e_2 = electrical charge particle 2
r = particles center distance (see figure 4.10)

Film formation will take place when the driving forces are larger then the resisting forces, thus:

$$F_{st} + F_c + F_{vdw} > F_w + F_c \qquad \text{(equation 4.3)}$$

Brown's theory is applicable for latex with small particles. Film formation of latex with larger particles (like styrene –butadiene copolymer) can not be explained. Vanderhoff, Tarkowski, Jenskins and Bradford developed a theory that can explain film formation from larger particles as well [2]. Within the framework of this thesis, Brown's theory gives enough insight in the film forming process, and therefore other theories will not be discussed.

On the one hand, film formation is a positive thing in prepreg processing. In powder processing (see section 2.4), an additional process step is needed to prevent powder from falling off the fibres. The formation of a coherent film makes this step unnecessary.

On the other hand, film formation can cause problems during drying. If film formation at the surface takes place when the inside is still wet, the drying rate will slow down considerably.

Impregnated prepreg, therfore, has to be dried at moderate temperatures in the beginning. At the end, the temperature must be raised to the minimum film formation temperature (MFFT), otherwise only dry powder will be present on the mat that can easily fall off.

The mats impregnated with Acronal 12 DE and ABS were dried during 30 minutes on 60 °C. The last 30 minutes the temperature was raised to 80 °C (MFFT) for Acronal 12 DE mats and 90°C for ABS impregnated mats. Drying took place in a hot air oven. Other drying methods, like microwave, IR, or RF will probably generate higher drying speeds because they heat up the material more evenly. This will be discussed in chapter 7 but is not tested in the framework of this research.

Migration; Migration is a second important aspect in drying latex impregnated fibre material. During drying, the inside of the mat is wetter than the outside. This causes particle migration to the outside of the mat. The latex particles are too small to be entrapped within the structure of the mat and the water carries them away. The result is a higher particle concentration on the outside of the mat. This can be avoided by drying at moderate temperatures or choosing a drying method that heats the mats evenly over the thickness of the mat(IR, microwave, RF). These methods reduce the moisture gradient, which is the cause of particle migration.

Pressing

To obtain complete consolidation, the impregnated mats have to be exposed to heat and pressure. For this purpose, a small mould was created. The mats were cut by scissors in pieces of 10 by 10 cm. Film formation prohibited latex particles from falling off. Four pieces were stacked, all in the same direction indicated by the felt-tip. This package was placed in the mould. A piece of teflon was placed both on the top and the bottom of the stack to ascertain easy release from the mould.

The mould was placed in a hot -platen press. Heat and pressure were applied using the cycle shown in figure 4.11 and figure 4.12. Temperatures were kept near 200° C to avoid fibre damage.

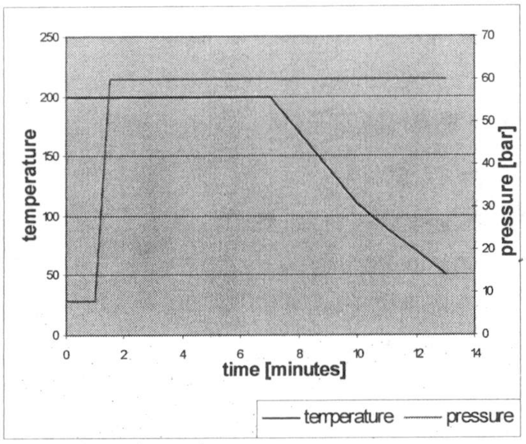


Figure 4.11: Temperature [°C] and pressure cycle for ABS/flax mat laminates

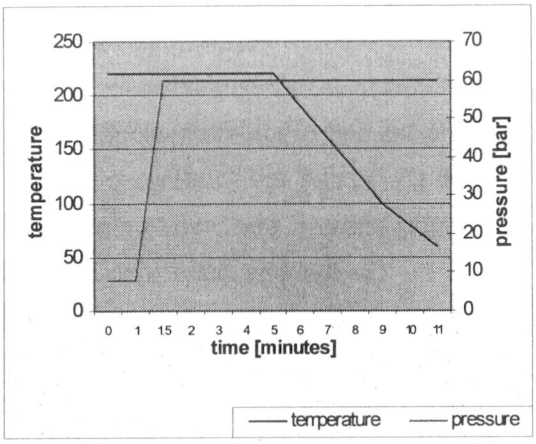


Figure4.12: Temperature [°C] and pressure cycle for Acronal12DE/flax mat laminates

4.3 Conclusions

Important conclusions that can be drawn from the preceding sections are:

- Properties of material used in this research are less than for ordinary ABS grades due to the surplus of polybutadiene.
- Moisture content in the flax mat is around 10% by weight
- An even latex particle distribution was obtained using 'washing and squeezing'. Paint roller impregnation resulted in an uneven distribution of particles
- ABS latex particles are small enough not to be filtered by the mat
- Latices form a continuous film when dried above the minimum film formation temperature. This can slow down drying speed but prevents polymer from falling off the mat.

5. Mechanical characteristics of latex flax composite laminates

In chapter 4 the processing route for flax mat reinforced ABS and Acronal 12 DE laminates was described. These laminates were subjected to flexural tests to find their mechanical characteristics and evaluate the possibilities for these materials for use in structural components. The first section takes a look at the tested specimen and test method. The concept of flexural strength and flexural modulus is discussed in section 2. The results of the test are given in section 3.

5.1 Tested specimens

Several Acronal 12 DE and ABS laminates were processed, all having different fibre volume content.

Rectangular specimen were cut from the laminates using an ordinary metal saw. This gave good control over specimen shape. The bandsaw turned out to be to rough, resulting in irregular shaped, coarse specimen. These specimen were not used for testing. Because of the anisotropic character of the laminates, the specimen were all cut in the same material direction. The small irregularities in the specimen surfaces were sanded using ordinary sand paper.

All laminates have a name starting with ANF (for Acronal 12 DE laminates) or ABSF (for ABS laminates), followed by the fibre volume content (example: ABSF30 is an ABS laminate containing 30% of flax fibres).

At least 4 specimens were used for each test and subjected to ISO 178, a three point bending test. This test is performed by placing a specimen over two supports and loading it at midspan. (see Appendix G)

5.2 Theoretical background for composite material calculations

If fibres and matrix are joined into a composite material (see figure 5.1), the stiffness of this composite can be theoretically calculated using the rule of mixture:

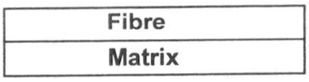


Figure 5.1: simplified composite structure

$$E_c = E_f V_f + E_m V_m$$
$$\sigma_c = \sigma_f V_f + \sigma_m V_m \qquad \text{(eq 5.1)}$$

In which:

E_c = modulus of elasticity of the composite

E_f = modulus of fibre material

V_f = Volume fraction of the fibres

E_m = modulus of elasticity of the matrix

V_m =Volume fraction of the matrix

σ_c = ultimate composite stress

σ_m= ultimate matrix stress

σ_f = ultimate fibre stress

This equation assumes a unidirectional allignment of the fibres. In a mat however, the fibres are randomly orientated. Equation 5.1 has to be corrected using the orientation factor η_0. The rule of mixture than becomes:

$$E_c = \eta_0 E_f V_f + E_m V_m$$
$$\sigma_c = \eta_0 \sigma_f V_f + \sigma_m V_m \qquad \text{(eq 5.2)}$$

For a random mat, η_0 has the value 0.38 [Klunder 1990].

With Vf + Vm = 1; eq 5.2 becomes:

$$E_c = (\eta_0 E_f - E_m)V_f + E_m$$
$$\sigma_c = (\eta_0 \sigma_f - \sigma_m)V_f + \sigma_m \qquad \text{(eq 5.3)}$$

These equations show that composite properties in theory are linearly dependent on fibre volume fraction V_f.

E_m, E_c, σ_m, and σ_c were determined by a three point bending test. The result of this test is a stress/strain diagram, as shown in figure 5.2.

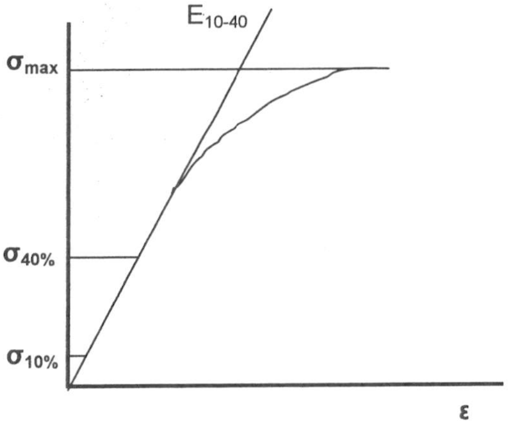


Figure 5.2: Schematic stress-strain curve

E is determined by calculating the slope of the stress-strain diagram between 10–and 40% of the maximum stress. The 10% boundary eliminates the mostly unreliable data that is obtained at the start of the test. Most materials are used below 40% of their maximum stress, therefore this boundary is chosen as the upper limit.

The values for σ_m and σ_c are defined as the maximum stress (σ_{max}) shown in figure 5.2. Once E_m, E_c, σ_m, and σ_c are known, the apparent fibre stiffness ($E_{f,eff}$) can be calculated using a rearranged form of equation 5.3:

$$E_{f,eff} = \frac{E_c - (1 - V_f)E_m}{\eta_0 V_f} \qquad \text{(eq 5.4)}$$

This quantity makes it possible to compare fibre effectiveness for laminates at different fibre volume content.

Because the validity of the rule of mixtures for composites with random mats can be doubted and the value for η_0 has not been tested for the flax mat, eguation 5.4 will only be used for a qualitative comparison of composites at different fibre volume content with one type of matrix and not for comparison of AN 12DE and ABS composites.

5.3 Test results

Acronal 12 DE/flax

Table 4.2 shows the test results for the Acronal 12DE/Flax laminates at different fibre volume content (V_f). The number in the name of the different laminates indicate the fibre volume that was aimed at during the impregnation process, using the method described in appendix F. The second column shows the fibre volume content that was actually achieved. For ANF20, ANF30, ANF40, the intended and actual value are allmost the same. This proves that AN 12DE latex prepregging gives good control over fibre volume content.

laminate	V_f [%]	G_f [%]	σ_{flex} [MPa]	$E_{f10\text{-}40}$ [GPa]	E_{eff} [GPa]
Acronal 12DE	0	0	90.2	3.08	n.a.
ANF10	12.9	15.8	105.1	6.4	75.8
ANF20	20.4	24.3	117.2	7.9	75.3
ANF30	30.4	34.8	118.5	9.5	63.5
ANF 40	39.8	44	94.5	7.3	35.9
ANF50	47.4	50.9	75.7	5.2	19.7

Table 5.2: flexural properties of Flax/Acronal 12DE laminates

During impregnation of the ANF10 material, the mat was not able to absorb enough latex. This explains the difference between the intended and actual V_f. In this case, latex with a higher solid content should have been used. During impregnation of the ANF50 mats, it was not possible to squeeze out enough latex from the impregnated mats. Therefore a lower fibre volume was obtained. In this case, a latex with lower solid content should have been used.

Figure 5.3 shows the stress-strain diagram for pure Acronal 12DE and ANF30. The reinforcing effect of the fibres is evident. Flexural strain of the reinforced material is reduced because of the low ultimate strain of the fibres in the material. Pure AN 12DE shows a high ultimate strain compared to pure acrylics.

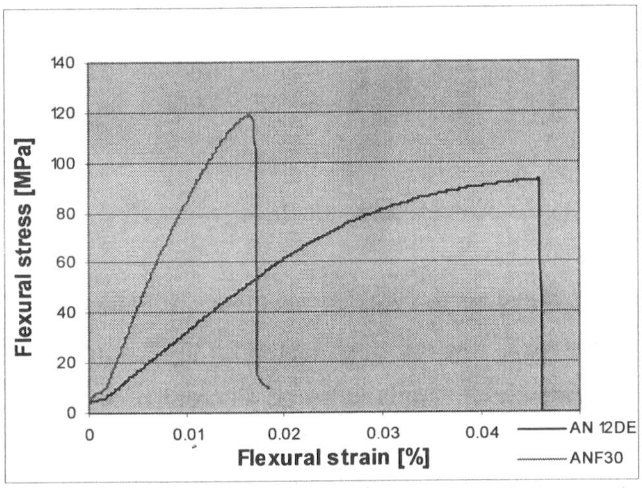


Figure 5.3: Stress-strain diagram for reinforced and unreinforced Acronal 12DE

Thermoplastics with low ultimate strain (like pure acrylic latices) can give problems in composites: the matrix breaks before the ultimate strain of the fibres is reached and the fibres in the composite are not used optimally. This problem is not expected to occur in AN 12DE laminates

Figure 5.4 shows the maximum flexural stress at different values for V_f. The highest, lowest and average value of all laminate specimens are indicated in the figure (average indicated with a dot). The differences within the specimens of the different laminates are high, especially for ANF20 and ANF30. Fibre flow during pressing due to pressure differences in the mould could be an explanation. The flow causes V_f variations within the specimens of each laminate. Local contamination of the mats (i.e. wood shives) or voids could be another explanation. The reinforcing effect of the fibres on σ_{flex} is limited: at 13% fibre content, σ_{flex} is raised by 16%, maximum stress is reached around 25% fibre volume and is only 33% higher than for the unreinforced thermoplast. Premature matrix failure caused by limited matrix strain can be excluded as a possible explanation, as discussed earlier.

Limited fibre/matrix compatibility is the most probable explanation. The matrix is not capable of transfering the stresses to the fibres effectively. The fibres can therefore be seen as a filler material more than as a reinforcement material.

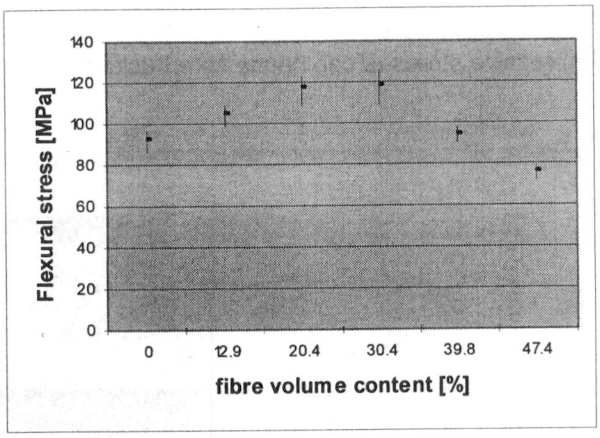


Figure 5.4: Flexural stress at different fibre volume content for ANF laminates

When fibre content is over 30%, σ_{flex} drops rapidly. At 40% V_f, σ_{flex} is almost on the same level as for unreinforced AN 12DE. This can be explained by bad wetting. The matrix is not capable of replacing the space between the fibres completely.

Because impregnation by the latex gave an even distribution in the flax mat (see figure 4.3), bad wetting was not expected. A possible explanation could be a high viscosity of the thermoplast. Although small particles are evenly distributed througout the mat, viscosity is so high that, even at high pressures, the particles can not flow together into one solid matrix structure. During pressing of the NFRP material, no flow of matrix material out of the mould could be observed. This is a possible proof for the theory described.

The dry spots in the material, as can be seen on the surface of the ANF50 laminate (figure 5.5), have an decreasing effect on flexural stress in three ways:

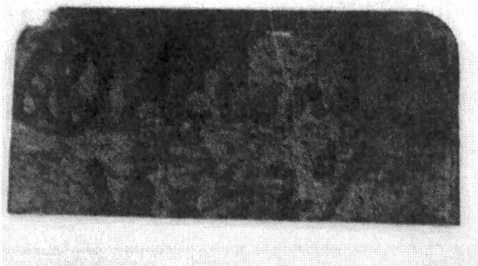


Figure 5.5: dry spots in ANF 50 laminate

1. Stresses have to be diverted to the outside of the dry spot. This can lead to stress concentrations close to the spot and causes premature matrix failure.

2. Dry spots decrease the effective surface area of the cross-section and are responsible for an increase of the total stresses.
3. The compressive stresses can cause fibre buckling in the dry spots.

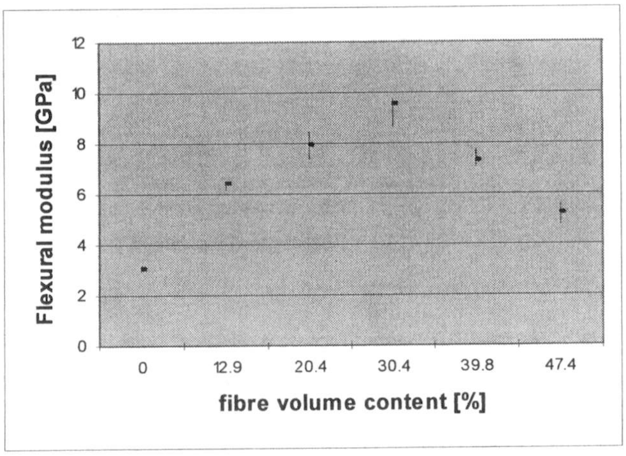


Figure 5.6: : Flexural modulus at different fibre volume content for ANF laminates

Figure 5.6 shows $E_{f10\text{-}40}$ for the different ANF laminates. The maximum value is reached in ANF30 and is 3 times higher than for the unreinforced AN 12DE. This is a much better result than for the flexural stress. The influence of bad fibre/matrix interaction on stiffness is clearly less than on flexural stress. Above 30% V_f, $E_{f10\text{-}40}$ drops to much lower values because present dry spots reduce the effective cross-section.

The last column in table 5.2 shows the effective flexural modulus of the fibres, calculated using equation 5.4. Fibre effectiveness decreases at increasing fibre volume, due to the introduction of dry spots.

In table 5.2, density, specific flexural stress ($\sigma_{flex,spec}$) and specific flexural modulus ($E_{f10\text{-}40,spec.}$) are given for the different ANF laminates and for a typical glass mat reinforced polyester with 30 % G_f (see table 2.1) , for comparison. Polyester was chosen because it has strength, stiffness and density comparable to that of AN 12DE.

If the polyester laminate (30% G_f) and ANF30 (34.8% G_f) are compared, it is evident that ANF30

laminate	specific weight [g/cm^3]	$\sigma_{flex,spec}$ [10^6 m^2/s^2]	$E_{f10\text{-}40,spec}$ [10^3 m^2/s^2]
ANF10	1.2	88	5.3
ANF20	1.22	96	6.5
ANF30	1.26	94	7.6
ANF40	1.29	73	5.7
ANF50	1.32	57	4.0
Polyester/glass mat	1.5	120	7.3

Table 5.2: specific properties of ANF laminates

gives worse strength and only sligthly better stiffness results. Weight savings are therfore no possible usin the ANF laminates.

ABS/Flax

Table 5.3 shows the test results for the ABS /Flax laminates at different fibre volume content(V_f). Like with the AN 12DE laminates, the actual fibre volume are close to the values aimed at. This shows that ABS latex prepregging offer good control over V_f.

laminate	V_f [%]	G_f [%]	σ_{flex} [MPa]	E_{f10-40} [GPa]	$E_{f,eff}$ [GPa]
ABS	0	0	33.4	1.04	n.a.
ABSF20	19.6	25.9	70.8	3.03	29.4
ABSF30	30.3	37.8	110.3	6	45.8
ABSF40	42.1	49.2	119.4	7.3	41.1
ABSF50	48.3	54.8	99.3	4.66	22.46

Table 5.3: Flexural properties ABS/flax laminates

Figure 5.7 shows the stress-strain diagram for pure ABS and ABS40. The reinforcing effect of the fibres is evident. Both flexural stress and flexural modulus are raised considerably. ABS has a much higher ultimate strain than AN 12 DE (see figure 5.3) and premature matrix failure in the ABS composites is therefore not to be expected.

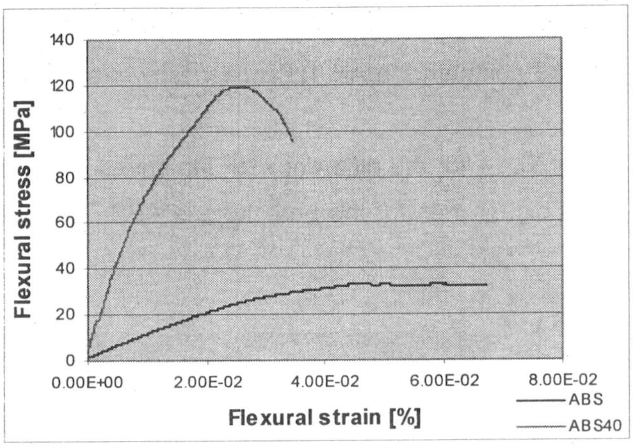


Figure 5.7: Stress-strain diagram for reinforced and unreinforced ABS

Figure 5.8 shows the maximum flexural stress at different values for V_f for ABS laminates, similar to figure 5.4. The differences between the test specimens of one laminate are considerable and can be explained contamination of the mat and variation of V_f in the laminate caused by pressure differences in the mould. The differences are larger for high V_f laminates because local dry spots are more likely to occur. The reinforcing effect of the fibres on σ_{flex} is much higher than for the ANF laminates. Flexural stress for ABS20 is more than two times higher than for unreinforced

ABS. The maximum is reached around 40% V_f and is more than 3.5 times the value for pure ABS. This can partly be explained by the much lower σ_{flex} value for ABS compared to AN 12DE. Fact is however, that σ_{flex} for ABS30 is close to σ_{flex} for ANF30, so the low σ_{flex} value for ABS can not be the only explanation. ABS is clearly better capable of transferring the stresses to the fibres. This indicates a better bond between fibre and matrix.

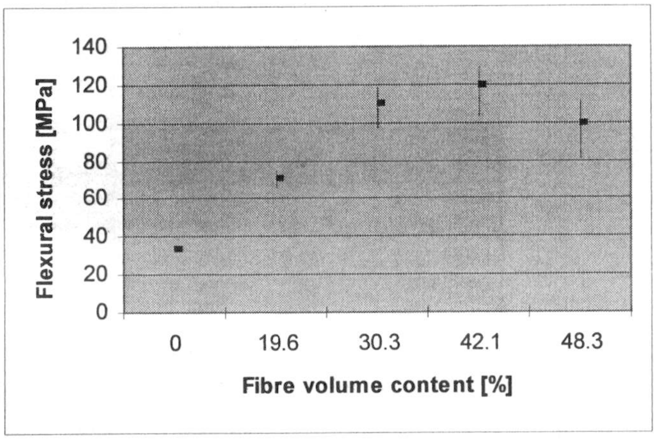


Figure 5.8: Flexural stress at different fibre volume content for ABSF laminates

When comparing figure 5.4 and 5.8, it can be noticed that higher V_f values can be used in ABS laminates. ABS40 gives the best flexural properties and shows no dry spots on the surface. ANF40 , on the other hand, has worse flexural properties than pure AN 12DE and shows many dry spots on the surface. ABS is better able to wet out fibres at higher V_f. This can be explained be the low viscosity of ABS compared to AN 12DE (viscosity of acrylics in general is much higher than for ABS grades).

Figure 5.9 shows $E_{f10\text{-}40}$ for the different ANF laminates. The maximum value is reached in ABS40 and is 7 times higher than for the unreinforced ABS. The last column in table shows

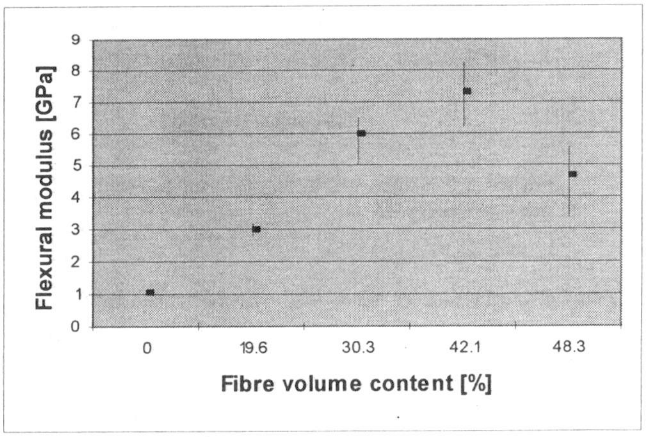


Figure 5.9: : Flexural modulus at different fibre volume content for ABSF laminates

the effective flexural modulus of the fibres, calculated using equation 5.4. This figure shows a large drop in fibre effectiveness around 40% V_f.

In table 5.10, density, specific flexural stress ($\sigma_{flex,spec}$) and specific flexural modulus ($E_{flex,spec.}$) are given for the different ABS laminates and for a typical glass mat reinforced ABS with 20%G_f (see table 2.1) for comparison (in theory 20% G_f corresponds with 9.5% V_f for this composite, as indicated in table 5.3).

laminate	specific weight [g/cm^3]	$\sigma_{flex,spec}$ [10^6 m^2/s^2]	$E_{f10\text{-}40,spec}$ [10^3 m^2/s^2]
ABSF20	1.10	64.32	2.75
ABSF30	1.15	95.59	5.20
ABSF40	1.21	98.47	6.02
ABSF50	1.24	79.87	5.87
ABS/glass mat (9.5%V_f)	1.19	90.00	5.05

Table 5.3: Flexural properties ABS/flax laminates

Looking at $\sigma_{flex,spec}$, both ABS30 and ABS40 perform better than ABS/glass, looking at $E_{flex,spec}$, all laminates except for ABS20 perform better. So weight savings are possible, but at much higher fibre volumes. Flexural properties of the ABS used in this research were low because of the high polybutadiene content. Normal ABS is around 2 times as strong and 2,5 times as stiff. The use of this kind of ABS will give better composite properties and will certainly give more weight saving opportunities.

5.4 Conclusions

Important conclusions that can be drawn from the preceeding section are:

- Latex prepregging offers good control over fibre content

- Flax fibres have limited effect on σ_{flex} of the AN 12DE laminates, probably due to bad fibre/matrix interaction.

- σ_{flex} is enhanced by a factor 3.5 for ABSF laminates

- $E_{f10\text{-}40}$ can be enhanced by a factor 3 for ANF laminates and a factor 7 for ABSF laminates

- Maximum fibre volume is 30 % for ANF laminates and 40% for ABSF laminates

- Compared to glass mat reinforced polyester, ANF laminates have no weight saving potential

- Compared to glass matt reinforced ABS, ABSF laminates have interesting weight saving potential

6. Bonding of natural fibres to thermoplastic matrices

A good bond between fibre and matrix is essential to obtain a good composite that uses the full potential of the reinforcing fibre. The first step in achieving a good bond is to bring the fibre and matrix in close contact. The concept of wetting makes it possible to quantify this process and is discussed in section 6.1. The problems involved in the hydrophilic character of the fibres and the hydrophobic thermoplastics are discussed in the same section.

The use of a compatibilizing agent, MAPP (Maleine Anhydride modified PP) in achieving a better bond has proven to be effective. Section 6.2 explains why and gives some results that were found in literature.

One of the methods to apply MAPP to fibres is the use of a MAPP emulsion. Such an emulsion could be added to latex used in NFRP's prepreg processing so fibre sizing and impregnation can be done in one step. An experiment is done to determine the effect of MAPP emulsions on composite properties (section 6.3).

6.1 Surface energy, wettability and adhesion

Wetting is defined as the process whereby a liquid if brought into contact with a solid, displaces the vapor, so that a stable contact is formed between the three faces [30].
The degree of wetting can be quantified by measuring the contact angle. As shown in figure 6.1 the contact angle is defined as the angle between the normals to the solid and liquid surface (as measured in the gas) at the point of interest along the three-phase line.

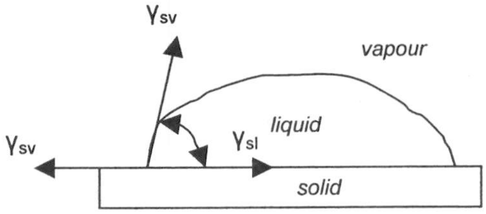


Figure 6.1: Contact angle as a measure of wettability

The contact angle can be related to the surface energies of the three faces by Young's equation:

$$\cos\theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \qquad \text{(Equation 6.1)}$$

Θ = contact angle

γ_{sv} = solid/vapour interfacial energy

γ_{sl} =solid/liquid interfacial energy

γ_{lv} = liquid surface tension

Best wetting takes place if $\theta = 0$. This situation is possible if γ_{sv} is high and γ_{sl} and γ_{lv} are low. The liquid totally spreads out achieving a full wet out of the solid.

If $0° < \theta < 90°$ the liquid only partly wets the solid. In the third case, $90° < \theta < 180°$, the liquid doesn't wet out the solid. It is clear from Young's equation that this situation is favored by high surface tension liquids on low surface energy solids.

Measurement of the contact angle for flat surfaces is quite simple, but for fine, anisotropic structures like fibres it is difficult because fibre geometry and porosity influences the results. This is why an alternate method based on the Wilhelmy equation was developed. The Wilhelmy equation:

$$F = p\,\gamma_{lv}\cos\theta \qquad \text{(equation 6.2)}$$

relates the force F, exerted on the fibre to p (the perimeter of the fibre), the liquid surface tension and the contact angle θ. The wetting force is obtained by measuring the apparent weight increase when the fibre contacts a liquid of known surface tension. Because these forces are very small, microbalances have to be used.

The work of adhesion is, by definition, the work required to reversibly separate one bulk phase (i.e., a liquid) from another bulk phase (i.e., a solid).

DuPré developed the following relationship for work of adhesion W_a:

$$W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \qquad \text{(equation 6.3)}$$

Combination of equations (1) and (3) results in:

$$W_a = \gamma_{lv}\,(1 + \cos\theta). \qquad \text{(equation 6.4)}$$

According to the adsorption theory the work of adhesion (W_a) consists of four different types of interactions:

$$W_a = W_d + W_p + W_h + W_{ab} \qquad \text{(equation 6.5)}$$

W_d is the work done by the *dispersive forces*. These forces are a result of momentary asymmetrical electron distributions in atoms. This distribution leads to dipolarity of the atom. This affects neighbouring atoms. The attraction between atoms as a result of this is weak.

W_p is a result of *polar forces.* The difference in electronegativity between atoms can result in molecules that have an asymmetrical electron charge distribution. A molecule with this character is called a dipole. Different dipoles are attracted to each other and form a bond.
The dispersion and polar forces together form the van der Waals forces.

W_h refers to the work done by the forces caused by the *hydrogen bonds*. When a hydrogen atom is attached covalently to an atom with high electronegativity such as O and N a strong dipole is created. Other atoms with high electronegativity are attracted by this dipole. The hydrogen bonds are strong bonds. Natural fibres have a lot of hydroxyl groups and are therefore capable of hydrogen bonding to suitable atoms.

W_{ab} is the work done by the forces that are a result of acid-base interactions. These interactions cover any interaction that involves sharing of an electron pair. The hydrogen bond is in fact aswell caused by an acid-base interaction, but it has a special name, because of its importance.

Conclusion: good wettability depends on the surface energy of the materials involved in the bond. A high wettability results in a high W_a value and therefore in a better bond according to the given theory.

6.2 A better fibre-matrix bond using MAPP

Natural fibres are polar, hydrophilic solids. A typical contact angle for a flax fibre in water is 70°. Polyolefins (PP, PE) and other synthetic polymers frequently used in composites are hydrophobic. A typical contact angle for PP in water is 97°.

This difference in polarity makes wetting of natural fibres by thermoplastics very difficult (γ_{sl} in equation 6.1 is high) and a poor bond between the fibres and the is the result. To create a better bond, it is necessary to make the fibres less polar so γ_{sl} is reduced. This can be done using a compatibilizing agent.

A compatibilizing agent is a molecule that contains a function F at one end that is capable of reacting with the hydroxyl groups on the natural fibre. The other end contains either an alkyl chain or a polymeric chain with a structure similar to that of the matrix.
There are many different functions F available that can react with the hydroxyl group. The functions that are most widely used are carboxylic anhydrides and isocyanates. The nonpolar part of the agent contains a small alkyl group or a polymeric structure such as functionalized polypropylenes.

MAPP is a compatibilizing agent that is often used to improve natural fibre bonding to PP (polypropylene) and PE [10, 12, 19, 22]. It is a molecule with on one end Maleic Anhydride, and on the other end a PP chain. The PP chain is much smaller than the PP matrix chain length.This makes it possible for the MAPP molecule to migrate to the fibre surface. Here the MA-side provides polar interactions, but can also covalently link to the hydroxyl groups on the natural fibre as can be seen in figure 6.2.The PP segment of the MAPP molecule interacts with the matrix material through chain entanglement. Stresses on one chain are transmitted to the other entangled chains. The chain length of the MAPP molecule has a major influence on the quality of the interface. If the chains are too short, there is little chance of entanglement between chains and they can easily slide past the PP chains. If the chains are too long, they entangle with the PP molecules without having the time to reach the fibre surface.

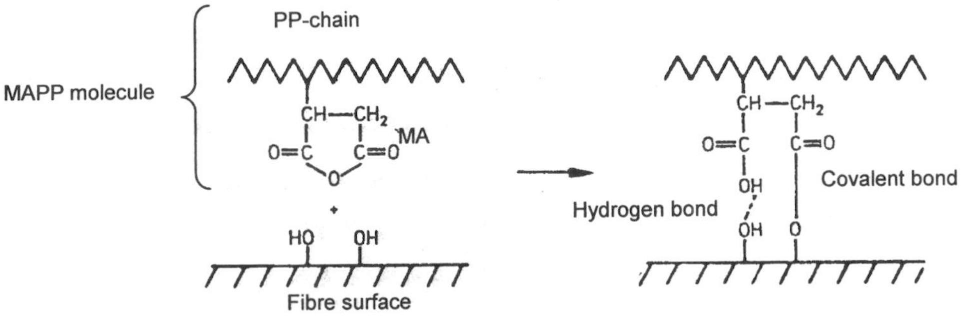


Figure 6.2: Bonding of MAPP to the natural fibre

In all the MAPP solutions a certain amount of free MA is present. This MA bonds to OH-groups on the fibre and thereby reduces the interaction between MAPP and the fibre.

There are many types of MAPP available on the market. Table 6.1 lists some of the MAPP products and their supplier.

Product name	Supplier
Epolene 43	Eastman Kodak
Hercoprime Hg 201	Himont
Hostaprime HC5	Hoechst
Exxelor PO 1015	Exxon chemicals
Polybond PB-3002	BP Amoco

Table 6.1: MAPP products and suppliers

These products vary not only in MA content (0.2- 6-wt %) and by the molecular weight of the polymeric part but also by the distribution of the grafted moieties. There are large differences in the reported improvements realised with these products. In general, tensile- and flexural strength were improved by 20-60 % and tensile- and flexural modulus remained unchanged.

There are three different ways to treat fibres with MAPP:

- Solution
- Fibre/film
- Emulsion

Sizing of the fibres is usually done using MAPP in solution. A certain amount of MAPP is dissolved in a solvent (i.e. toluene). The natural fibres are immersed in this solution, washed and dried to remove the solvent.

MAPP can also be incorporated in a film or polymer-yarn. During NFRP processing, the MAPP molecules can migrate from the matrix material to the fibres. The problem however is that relatively more MAPP has to be added, while during processing of the composite only a small percentage of the MAPP can find their way to the natural fibre surface. The MAPP- molecules that are not bonded to the fibre surface reduce tensile strength and stiffness of the composite.

MAPP molecules can also be processed into latex. Just like with the solution method, fibres are immersed in the latex and dried. Latices only contain water and no dangerous solvent like in the solution method. Sizing of natural fibres by these latices therefore better fit to the environmental friendly character of NFRP composites.

In chapters 4 and 5 the impregnation of natural fibres with latices has been investigated. MAPP latices could be mixed with these latices before fibre impregnation. This makes it possible to integrate the fibre sizing and impregnation step.

In literature no information about natural fibre sizing by MAPP latices was found.

Suitable sizings for ABS, for example MAABS, could not be obtained during the period of this research, therefore experiments were done with two different MAPP latices in Flax/PP composites. The results are given in section 6.3.

6.3 Effect of MAPP latices on NFRP characteristics

This section discusses the research done on the use of MAPP latices on the quality of a flax fibre reinforced polypropylene. First the materials used in this test will be discussed, followed by the processing aspects. Finally the results of the research will be given.

	Permanol 603	**AAP5**
Solid content [%]	34	30
Viscosity mPa.s	<250	<250
MAH content (%)	2.6	7.5
M_w	47000	12000

Table 6.2: MAPP latex properties

Materials

<u>MAPP latices</u>

Two types off MAPP latices were tested, both supplied by Dick Peters BV:

Permanol 603 and AAP 5. They were developed as a compatibilizing agent for PP filler like glass, talc and wood flour. Table 6.2 lists some important characteristics of these products.

Viscosity of both latices has a value in-between that of pure water (1mPa s) and linseed oil (500 mPa s) and impregnation problems are therefore not to be expected.

The two products differ in MAH content and molecular weight, two aspects having great influence on MAPP performance (see section 6.2). Grafting of MAPP requires a break down of

PP chains by a radicalisation process in the presence of an initiator. This means that a high MAH content coincides with low molecular weight and vice versa, as can be seen from table 6.2.

Both products could be diluted with water without causing destabilisation.

Matrix material

Both MAPP products were developed as a compatibilizing agent for PP fillers, therefore, polypropylene was chosen as matrix material in this research.

The PP used in this research was made of recycled PP products and delivered as a film of 0.5-mm thickness. Table 6.3 gives some important material properties that were obtained by testing:

material	σ_{flex} [MPa]	E_{f10-40} [GPa]	ε_{flex} [%]	T_m [°C]
PP	53.1	1.475	0.076	185

Table 6.3: PP properties

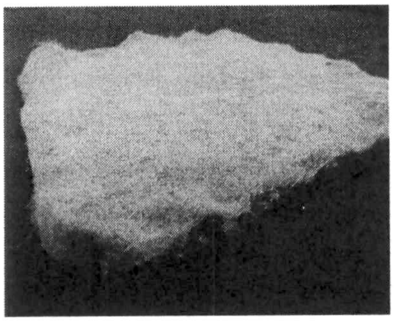


Figure 6.3: needle punched flax mat

Fibre characteristics

The same needle-punched flax mat was used as in chapter 4 (see figure 6.3).

Process aspects

The process aspects will be discussed in the following order:

- Mat impregnation
- NFRP processing

Mat impregnation

The mats were impregnated with 1,2 and 3% MAPP on fibre weight by immersion in a bath during 30 minutes. Excessive latex was squeezed out by hand. It was not possible to use the pure MAPP products, because after squeezing there was still far too much latex present on the mat. This problem is overcome by adding water to the latex and subsequently stirring. A 1% solid content latex was found to be most practical. The procedure described in Appendix C was used to deposit the desired amount of MAPP on the mat. After the mats were squeezed, they were dried in a drying oven on 80 °C for 1 hour.

NFRP processing

The impregnated mats were combined with the PP matrix using the filmstack method (see section 2.4) Four pieces of PP film were stacked in a sequential order with three mat layers. This resulted in a fibre volume content around 22% for the composite material. The stack was fixed using an ultrasonic gun. An aluminum mould was heated in a hot platen press. The temperature was measured by a thermo-couple attached to the inside of the mould. After reaching a temperature of 200°C, the mould was opened and the package was placed inside. To assure easy release from the mould, top and bottom of the package were covered by Teflon. After closing the mould, the material was heated at 5 bar for 3 minutes before applying the full pressure of 60 bar. After 13 minutes, cooling started. After reaching a temperature of 100°C, the mould was opened and the material removed.

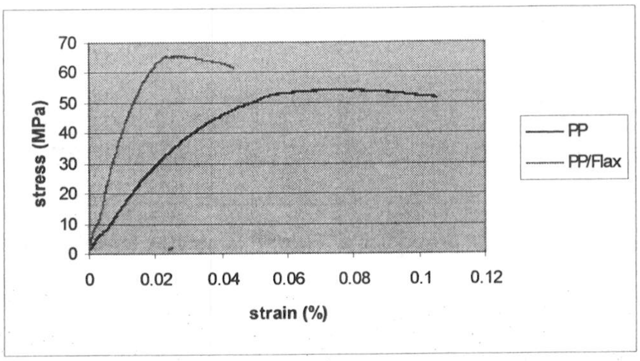


Figure 6.4: Stress strain curve for PP and PP/flax

Mechanical properties

To evaluate the effect of MAPP treatment on NFRP properties, flexural strength (σ_{flex}) and flexural modulus ($E_{10\text{-}40}$) have been determined. This has been done using ISO standard 178 (appendix G), a three point bending test. Beams have been cut from the pressed NFRP material using an ordinary iron-saw. At least 3 specimen have been cut from each NFRP plate.

Figure 6.4 shows a stress-strain diagram for unreinforced PP and flax mat reinforced PP (without MAPP). The maximum flexural stress and flexural modulus are raised, because part of the stresses in the material is transferred to the fibres. The increase is however less than could be expected in a composite that contains over 20% (Vf) of fibres. This can be attributed to the bad fibre-matrix interaction.

The failure strain decreases with the addition of fibres: Addition of the rigid fibre restricts the mobility of the PP molecules to flow freely past one another and thus causes premature failure. If the ultimate stress is reached, composite strength drops quickly.

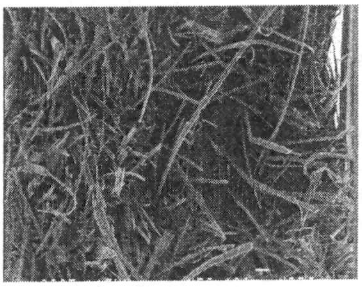


Figure 6.5: fracture surface of an untreated PP/flax laminate

Figure 6.5 shows a SEM photo of the fracture surface of the flax/PP composite without MAPP. A lot of dry fibres (i.e. without PP) visible. During bending, the fibre has been pulled out of the matrix because there was no good bond between the two.

Permanol 603

Table 6.4 reports the flexural strength $\sigma_{max,flex}$, the flexural modulus $E_{f10\text{-}40}$, and the maximum flexural strain $\varepsilon_{max,flex}$of the PP/flax laminates treated with different amounts of Permanol 603. Fibre volume fraction has a large influence on these properties. To make a useful comparison between several laminates, these values have to be converted to the values at a fixed fibre volume fraction (22% in this case). The result is given in the last column.

Material	**Permanol content [%]**	V_f [%]	σ_{flex} [MPa]	$E_{f10\text{-}40}$ [GPa]	$E_{f10\text{-}40\,(22\%)}$ [GPa]
Flax/PP	0	23.9	66.6	4.1	3.89
Flax/PP	0.5	24	75.0	4.0	3.88
Flax/PP	1	22	80.55	4.0	4.00
Flax/PP	2	22.8	78.3	4.0	3.91
Flax/PP	3	21.5	73.2	3.74	3.79

Table 6.4: Flexural properties of Flax/PP laminates treated with Permanol 603

Figure 6.6 shows the influence of Permanol content on flexural stress. The maximum flexural stress is reached at 1-% MAPP content, and is 21 % higher than for the uncoupled composite. Table 6.4 shows that V_f for this composite is low compared to the other composites. When this fact is accounted for, the raise of σ_{flex} is expected to be even more than 21%.

An explanation for the σ_{flex} increase, is a better bond between the fibre and PP matrix. The PP tails of the MAPP molecules are entangled in the PP chains, as explained in section 6.2. This promotes a better load transferring mechanism from matrix to fibres, resulting in a higher maximum stress.

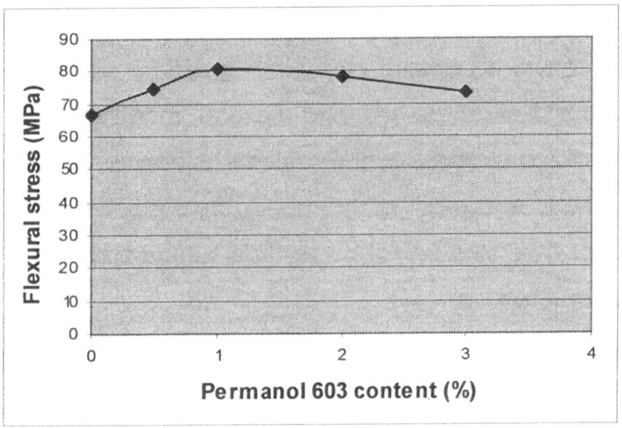


Figure 6.6: Influence of Permanol content on flexural stress

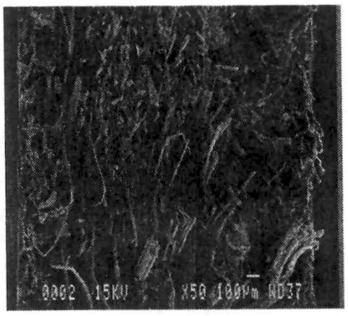


Figure 6.6: fracture surface of a Permanol treated PP/flax laminate

This theory is supported by figure 6.7 and figure 6.8: Figure 6.7 shows a SEM photo of the fracture surface of a treated fibre laminate (1% Permanol). Compared to the untreated fibre laminate (figure 6.5), the length of the fibres that have been pulled out of the matrix is much shorter. This is an indication for better fibre/matrix interaction.

Figure 6.8 shows the stress strain diagram for composites treated with 0 and 1% Permanol. After reaching the maximum stress, composite strength decreases much quicker for the treated than for the untreated laminate. The break behavior of the laminate with treated fibres is more dominated by the brittle fibres. This also indicates that a better bond.

Flexural stress decreases when more than 1% Permanol 603 is added (see figure 6.5). An explanation for this behavior is a combination of the following three cases:

- A surplus of Permanol causes the fibre surface energy to drop below the value for the PP matrix. This complicates wetout, thereby reducing the adhesion labor.
- MAPP-tails are entangled in neighboring MAPP-tails instead of in PP-matrix chains, causing earlier fibre slippage.
- The surplus of MAPP can not be bonded to the fibre surface, because all the accessible places are already in use. The non-bonded MAPP molecules act as a lubricant between the fibre and matrix.

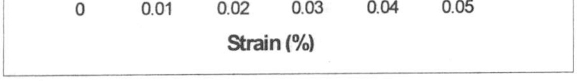


Figure 6.8: Stress-strain diagram for Permanol treated and untreated Flax/PP laminates

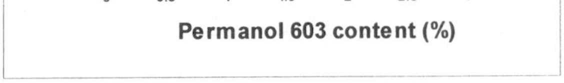


Figure 6.9: Influence of Permanol content on flexural modulus

Figure 6.9 shows the minimal influence of Permanol 603 on flexural modulus. Again there is a maximum around 1%. The value at this point is only 3% higher than for the untreated laminate. This can be explained by the calculation method for $E_{10\text{-}40}$. $E_{10\text{-}40}$ is not measured at the point of composite breakage (as is the case for σ_{flex}), but in the area between 10 and 40 % of the maximum stress (see section 5.2) The stresses in this area are apparently not high enough for fibre slippage to occur. As long as the fibre is attached to the matrix at several points, the slope of the stress-strain curve (see figure 6.8) is almost identical for the treated and untreated laminate. The two lines just start to diverge noticeable when 35% of the maximum stress is reached.

If more than 1% Permanol is added, E_{flex} drops, and between 2 and 2.5 % it even drops below the value for the untreated flax fibres! The possible explanations for this behavior are similar to those given for the drop in σ_{flex}.

AAP5

Table 6.4 reports the flexural strength σ_{flex}, the flexural modulus $E_{10\text{-}40}$, and the maximum flexural strain ε_{flex} of PP/flax laminates treated with different amounts of AAP5.
Again the stiffness recalculated to a fixed fibre volume is given in the last column.

Material	AAP5 content [%]	V_f [%]	σ_{flex} [Mpa]	$E_{10\text{-}40}$ [GPa]	$E_{10\text{-}40\,(22\%)}$ [GPa]
Flax/PP	0	23.9	66.6	4.10	3.78
Flax/PP	0.5	23	64.3	3.63	3.44
Flax/PP	1	21	64.9	3.05	3.05
Flax/PP	2	24	75.7	4.51	4.13
Flax/PP	3	22	70.6	4.03	3.91

Table 6.5: Flexural properties of Flax/PP laminates treated with AAP5

Figure 6.10 shows σ_{flex} as function of AAP5 content. The maximum flexural stress is reached at 2% AAP5 content and is around 12 % higher than for the untreated laminate. This is much less than the raise in flexural stress that was reached using Permanol 603. A possible explanation could be the fact that M_w for AAP5 is less than for Permanol 603. The shorter MAPP chains can not penetrate the PP chain of the matrix as deep as those of Permanol 603. This results in a less effective stress transfer from the matrix to the fibres. Figure 6.10 shows a decline of σ_{flex} after the

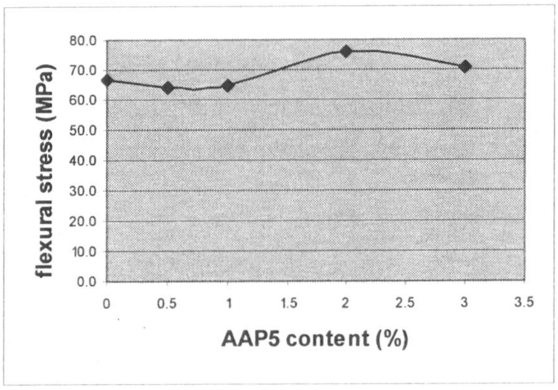


Figure 6.10: Influence of AAP5 content on flexural stress

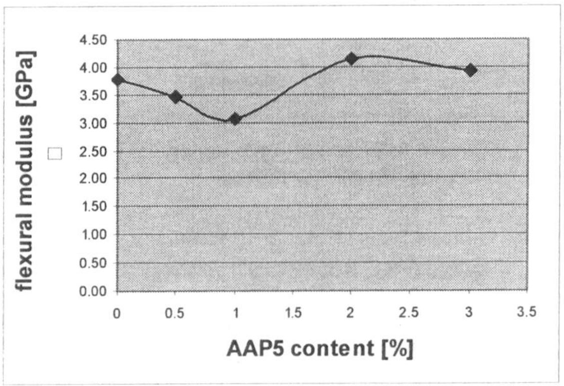


Figure 6.11: Influence of AAP5 content on flexural modulus

maximum is reached. This result was also found for the Permanol 603 laminate and can be explained by the same considerations. The drop in σ_{flex} before reaching the maximum however, was not observed in the Permanol 603 laminate.

This can also be explained by the short MAPP chains of AAP5. If only little AAP5 is added, the decrease in modulus by the lubricating effect of the short chains is not exceeded by the increase through better wetout and entanglement. At a certain point, these two processes having an opposite effect on flexural stress are equal. From this point, addition of more AAP5 improves flexural stress as shown in figure 6.12.

Figure 6.11 shows E_{10-40} as function of AAP5 content. Unlike for Permanol 603 treated laminates, AAP5 has a distinct influence. The maximum value is reached around 2% AAP5 content, and is 9% higher than for the untreated laminate. No explanation was found for this behavior. More striking is the decrease of 26% in E_{10-40} around 1% AAP5 content. A possible explanation could be that the short AAP5 PP chains increase the flexibility of the PP matrix to such an extent that matrix modulus is seriously effected.

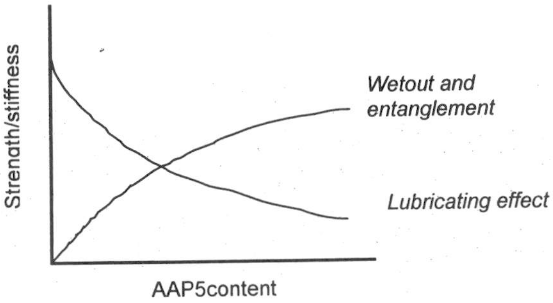


Figure 6.12: Wetout/entanglement and lubricating effect on laminate strength/stiffness

6.4 Conclusions

Important conclusions that can be drawn from the preceeding sections are:

- Emulsion sizings can be a good alternative for sizing solutions or sizing addition in fibres and granules
- By adding sizing emulsions to latices, sizing and impregnation could be integrated in one step.
- Sizing of flax fibers with MAPP- emulsions is easy, the emulsions can easily be diluted with water to treat the fibers with the right amount of MAPP.

- Flexural stress was raised 21% for Permanol treated laminates and 12 % for AAP5 treated laminates.
- Flexural modulus was raised 3% for Permanol treated laminates and 9% for AAP5 treated laminates.
- Maximum properties were achieved at 1% Permanol 603 content and 2% AAP5 content.
- If fibres are treated with MAPP amounts that differ from the ones given above, flexural properties can even get worse than for untreated fibres.

7. Latex prepreg processing on an industrial scale

This chapter discusses the latex prepreg technique as a processing technique on an industrial scale. To clarify this discussion, the chapter starts with a general description of the process route (7.1). The problems and possible solutions of the different process steps are discussed in the following sections: Section 7.2 discusses material storage and transport aspects, impregnation of the fibre material by the latex is discussed in 7.3. The major part of the costs of latex prepreg processing is caused by the drying step, that will be discussed in section 7.4. The final operations that are necessary before the prepreg can be transported to the customer are discussed in section 7.5.

7.1 Process route for latex prepregs

The process route for latex prepregs can be divided in several steps, as can be seen in figure 7.1

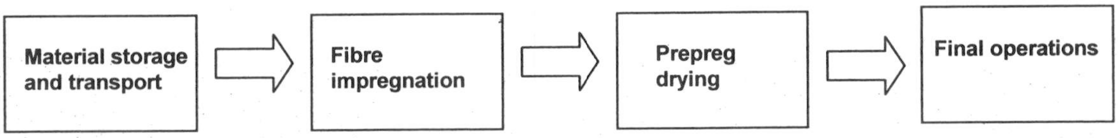


Figure 7.1: Process route for latex prepregs

Material storage and transport: Materials must be stored and transported without influencing quality negatively.

Fibre impregnation: In this step the latex is introduced to the fibre material. The process must be quick and result in a prepreg in which the latex particles are evenly distributed.

Prepreg drying: In this step the water has to be removed from the prepreg without damaging the fibres, latex particles, and particle distribution.

Final operations; This step includes the last operations necessary to make the prepreg ready for transportation to the customer.

7.2 Material transport and storage

There are no major problems involved in the transport and storage of latices [2]. Large amounts of latex can be transported in ordinary road tankers or train tankers. Smaller amounts can be transported in drums. Latex transport in pipelines is another possibility. Storage of latex on processing plants can be done in cylindrical tanks.

To maintain latex stability, homogeneity and composition, the following circumstances should be prevented [2]:

1. Drying out of residual latex
2. Freezing of the dispersion medium
3. Undue heating of the latex
4. Sedimentation or creaming of the latex
5. contamination

Ad 1) drying of latex is an irreversible process (see chapter 4). Dried residues in storage tanks, pipelines, processing equipment are difficult to remove. This problem can be overcome by good cleaning with water after use or a constant continuous refill.

Ad 2) freezing of latices leads to colloidal destabilization. Storage tanks and transport equipment must be insulated or even provided with heating devices.

Ad 3) undue heating of latices can also lead to colloidal destabilization and chemical changes. For some latices therefore proper cooling could be necessary.

Ad 4) creaming and sedimentation makes latex inhomogeneous. This makes a good control over latex polymer content difficult. Creaming and sedimentation can also lead to coagulation and the formation of a skin at the latex-air interface. These problems can be overcome by proper agitation. This also reduces temperature variations within the latex.

Ad 5) Contamination of the latex, by storage container material or extraneous sources, can cause discoloration and coagulation. Storage vessels made of glass, porcelain, stainless steel and several polymers are suitable. Beeswax and paraffin wax can be used as a coating of the inner surface of the thanks to prevent contamination. It also makes cleaning of the tanks easier.
Development of microorganisms can also cause problems, so small amounts of bactericides and fungicides are usually added.

Latices have a solid content ranging from 30-60 %. This means that 40-70 % of storage containers is filled with 'useless' material. In the case of dry granules storage however, a considerable amount of useless material is stored, namely air (In the case of spherical granules, this is 48 %).

Transference of latices from containers to other containers or process equipment is easy and can be done with small pumps. Small diameter pipes should be avoided to prevent blockage by coagulum or other sedimentation. Pumping equipment should not cause too much shearing, to prevent mechanical destabilization.

Transport and storage of natural fibre material doesn't cause major problems. The materials are normally delivered on rolls that can be transported on ordinary trucks.

Because natural fibres are susceptible to water, they should be stored in a relatively dry place. Excessive control over water content however is unnecessary because the fibre material is soaked with water in the impregnation step.

7.3 Fibre impregnation

During the impregnation step, latex has to be added to the fibre material. Figure7.2 and 7.3 show two principal methods to do this.

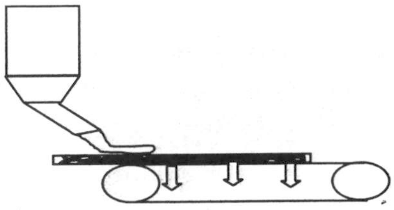


Figure 7.2: Pour impregnation

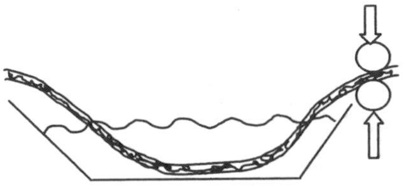


Figure 7.3: Bath impregnation

In pour impregnation, the desired amount of latex is poured out over the moving fibre material.

Bath impregnation involves the transportation of the fibre material through a latex bath.

Advantages of pour impregnation is the good support of the fibre structure by the transport band This prevents the structure from breaking by the weight of the latex in the case of a non-woven. There is also a good control over the amount of latex that is deposited.

Bath impregnation has the advantage of both sides of the web being exposed to the latex. This increases impregnation speeds. Because some fibre materials work as a filter, solid content of the latex bath could be influenced if the material moves through. Therefore good control over solid content is necessary. As shown in section 4.2, the flax mat didn't have this filtering effect.

From section 4.2 it was clear that impregnation speed with the aid of gravitational force only, is slow. Additional forces are necessary to obtain acceptable impregnation speeds.

In the case of pour impregnation this additional force could be obtained by using a wire screen with a filter material and applying vacuum.The small diameter of the latex particles however forms a problem. When the water is sucked from the mat, these particles are transported in the direction of the filter. This results in an inhomogeneous prepreg. Furthermore it is difficult to find a filter that keeps the particles out and water in at a sufficient speed.

In bath impregnation, additional pressure could be obtained by transporting the impregnated through squeezing rollers. These rollers give control over latex content as well.

7.4 Prepreg drying

Drying of impregnated fibre material is a major cost aspect of the latex prepreg process. The three major problems in latex drying are:

- *Large water content;* water content of latices is between 40 and 70 %
- *Film formation*; above a certain temperature (film-form temperature), the latex particles form a film that slows down water removal (see section 4.2)
- *Latex particle migration;* Latex particles are small and can easily migrate to the surface during drying. The result is a prepreg in which the polymer is divided inhomogeneous (see section 4.2).

These aspect will be used in evaluating the following drying methods [8,28]:

1. *Mechanical methods*
2. *Hot surface methods*
3. *Hot air method*
4. *Dielectric drying*
5. *Infrared drying*

Ad 1) Mechanical methods are the least expensive methods for removing large amounts of water. Water doesn't have to be evaporated in these methods. This makes the system design simpler and saves energy. Mechanical removal of water can be accomplished by squeezing the fibre material with rolls (mangles) or sucking the water throw a filter material using vacuum.
As already discussed in the previous section, the small diameter and therefore low filtering effect of the fibre materials gives problems to obtain a prepreg in which the particles are divided evenly.

Ad 2) In hot surface dryers, the impregnated mat material contacts a heated surface. The energy needed for evaporation of water is transported to the mat mainly by conduction. A well known example of this type of dryer is the cylinder dryer. It is used in the paper and non-woven industry as a second drying step after mechanical drying. The mat is transported over a cylinder that is heated from the inside by heated steam under pressure. The evaporate water at a rate of 10-25 kg/m^2 of contact surface per hour. Because heat transfer depends upon intimate contact between mat and cylinder surface, much effort is spent to keep these surfaces smooth, scratch- and corrosion free.

The use of these high capacity reliable cylinder dryers is interesting for latex prepreg processing. Latex film formation occurs first at the contact surface. Diffusion of water vapor through this film therefore isn't necessary (see figure 7.4).

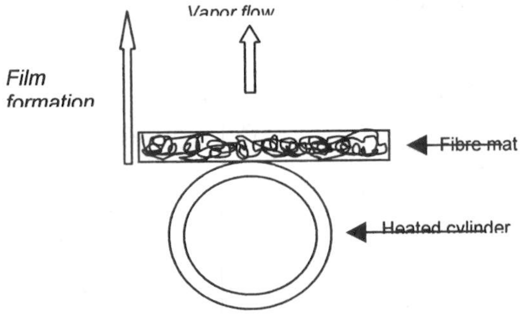


Figure 7.4: Cylinder drying

The heat transfer from the cylinder to the wet mat however, is complicated by the film formation because of the low heat conduction coefficient of dried polymers compared to wet substances. Particle migration is also a problem while the water vapor tends to bring the particles to the outer surface of the mat.

Ad 3) In hot air methods, heat is transported from a heated gas to the mat by conduction and convection. An industrial application is a Through- dryer. In this dryer, the mat is transported over a porous metal roll. Hot air is blown into a hood surrounding the roll. By applying vacuum at the inside of the mat, the hot air is drawn through the mat. Evaporation rates are higher than for cylinder drying because the air flow not only contacts all fibres, but also carries away water vapor from the mat. Typical values are 20- 400 kg/m^2 per hour.

The process is not suitable as a first dry step for latex prepregs because the high water content obstructs air flow. Film formation and particle migration problems are less because the mat is heated more evenly. Mechanical complexity of these dryers is greater than for cylinder dryers. The energy costs per unit of water removed are higher, while the amount of water evaporated per m^2 or per Euro of capital investment is higher.

Ad 4) Dielectric drying results when heat is generated by the application of electromagnetic fields. Microwave drying and radio-frequency (RF) drying are well known types of this method. They offer advantages in drying large diameters particles or materials that are not particulate. In these cases, heat input by convection, radiation, or conduction is rather inefficient compared to dielectric heat that generates heat from within the product. Compared to other drying methods, dielectric drying is clean, gives a better product quality and uses less floor space. RF and microwave are used in the paper-and board-using industry to dry out water based adhesives (on latex basis) and also in the textile industry. Both types use around 2kWhr/kg of evaporated water. The economic barriers to applying microwaves and RF industrially have historically been attributed to high capital equipment and maintenance costs. However, over the last several years, these economic barriers have crumbled. Equipment costs are now a fourth of what they were in the mid eighties and energy efficiency has increased over 150 %.

Dielectric drying is an interesting drying process for latex prepregs. It can be used for very wet mats (more energy is absorbed at high water content). Because the material in heated from within, film formation is not a problem using this method. Particle migration is also less, because the material is heated more evenly.

Ad 5) Infrared (IR) drying is accomplished by electromagnetic radiation. It has a limited penetration depth and is particularly interesting for drying surface coatings, paper and textiles. Infrared radiation can be generated in two ways: by passing an electric current through a resistance or by heating a ceramic plate with a burning gas. The plates emits the radiation. Drawback of IR heating is the high price for electricity. Gas radiation heating is not capital intensive. Around 60% of the energy supplied by the gas is converted into IR energy. A typical value for IR dryers is 50 kW/m^2.

IR is a good method for latex prepreg drying. Like with RF and microwave, film formation and particle migration problems are reduced.

Besides choosing the right drying method, particle migration can also be reduced by using a colloidal stabilizer. During drying, this stabilizer becomes ineffective due to temperature raise before water can evaporate, causing the latex to coagulate. The coagulated particles are to large to migrate to the surface. This method is successfully used for acrylonitrile-butadiene copolymers used as a binder for nonwovens (Brénon, 1982).

7.5 Final operations

After drying, the prepreg has to be cut to a desired shape to make transport to the customer possible. This can be done by ordinary cutting machines that are in use in the textile industry (cutting carpets) or in the composite industry (cutting of GMT) and will not cause problems.

The prepreg can be delivered in following two ways:

- Stack of plates
- Roll

Most of the prepreg material used in the automobile industry is delivered in a stack of plates. These plates are created by transporting the dried prepreg through a double-belt press. The polymer particles are melted and pressed around the fibres. This reduces the necessary flow length in the final product processing step thus having a positive effect on the cycle time.
Because polymer particles are well distributed in the dried prepreg material, less pressure and heat can be applied in the double-belt press compared to GMT prepreg production. Maybe even heated calendar rolls can be used instead of the expensive double-belt press.

If the polymer particles in the latex are no to brittle, the prepreg can be delivered on a roll. Research on the impregnated ABS/flax mat showed that film formation prevents latex particles from falling of during rolling. Prepreg rolls could be interesting if many different sizes are required in the product processing step. Because the impregnation of the prepreg is less than in the case of plates, cycle times for this material will be higher.

7.6 Conclusions

Important conlusions that can be drawn from the preceeding sections are:

- Transport and storage of latices is no problem as long as temperature of the latex is controlled and contamination or creaming is prevented.

- Pour and bath impregnation can both be used to deposit latex on the fibres, additional pressure to evenly distribute the latex in the mat can be supplied by vacuum or squeezing rollers.

- In theory, dielectric and IR drying methods are suitable for drying latex prepreg. These methods reduce drying time because the formation of a film in an early stage is avoided. Particle migration is reduced, having a positive influence on prepreg quality. Both methods are already used extensively in paper, textile and non-woven industry, so standard equipment can be used.

8. Conclusions and recommendations

8.1 Conclusions

Latex prepregging is an interesting alternative for common processing techniques

- No dangerous solvents are needed.
- Less fibre degradation during the prepreg process, because you don't need to melt the polymer particles.
- The small latex particles can easily enter fibre structures like yarns and mats.
- Viscosity of latices is low, even if solid content is high.
- Film formation prevents powder from falling off the fibre material.

Suitable latices for natural fibre prepregs are hard to obtain or not optimized for use in composites

- Many plastics, like PP and PE, are not made by the emulsion polymerization process and, therefore, not available as a cheap latex.
- Many latices available on the market don't meet the requirements for latex prepregs because they are designed for other end uses .
- Suitable latices are often not available on the market, but only present as an intermediary product in the production process of plastic granules.
- Companies are very reserved with providing latices, because they are afraid of giving away secret product information.

ABS, PVC, High Impact Polystyrene (HIPS)and certain acrylics are interesting latices for use in natural fibre reinforced plastics

- They are made by the emulsion polymerization process and therefore relatively cheap.
- Processing temperatures are within the processing window for natural fibres .
- ABS and HIPS could reduce impact problems of natural fibre reinforced plastics (NFRP's), because of their good impact toughness.

Processing of flax mat prepreg material using AN 12DE and ABS showed good results

- There is good control over fibre volume. Flax mats can be impregnated to fibre volume contents between 20% and 40% without problems.
- Latex has to be squeezed into the mat to get an even latex particle distribution.

- The flax mat has no filtering effect on the latex, therefore latex can also be distributed in thicker mat structures.
- Latex particles are stuck to the mat and don't fall off when the material is bent or cut. This is accomplished by film formation of the latex.

Weight saving is possible using ABSF laminates

- Reinforcing effect of flax mat on flexural stress of AN 12DE is limited due to bad fibre/matrix interaction. The maximum flexural stress (118.5MPa) is only 33 % higher than for the unreinforced AN 12DE. Maximum flexural modulus , 9.5 GPa, is 3 times higher than for unreinforced AN 12DE .
- Flexural stress of ABSF laminates is improved by 350% [119.4 MPa] compared to unreinforced ABS, fibre/matrix interaction is clearly better than for ANF laminates. Maximum flexural modulus is 7 times higher than for unreinforced ABS [7.3 GPa].
- Maximum flexural properties are achieved at 30% V_f for ANF laminates and 40%V_f for ABSF laminates. ABS is better capable of wetting the fibre because of a lower viscosity.
- ANF laminates perform worse on effective stress and little better on effective stiffness compared to a polyester/glass composite.
- ABSF laminates effective stress and effective modulus are higher than for a comparable ABS/glass composite, but at higher fibre volumes.

MAPP emulsions allow easy adding of fibre sizing

- Emulsion sizings can be a good alternative for sizing solutions or sizing addition in fibres.
- By adding sizing emulsions to latices, sizing and impregnation could be integrated in one step.
- Sizing of flax fibers with MAPP- emulsions is easy, they can be easily diluted with water to size the fibers with the right amount of MAPP.
- Flexural stress was raised 21% for Permanol treated laminates and 12 % for AAP5 treated laminates.
- Flexural modulus was raised 3% for Permanol treated laminates and 9% for AAP5 treated laminates.
- Maximum properties were achieved at 1% Permanol 603 content and 2% AAP5 content.
- When fibres are treated with MAPP amounts that differ from the ones given above, flexural properties can even get worse than for untreated fibres.

Application of latex prepreg process on an industrial scale is possible

- Transport and storage of latices is no problem as long as temperature of the latex is controlled and contamination or creaming is prevented.
- Pour and bath impregnation can both be used to deposit latex on the fibres, additional pressure to evenly distribute the latex in the mat can be supplied by vacuum or squeezing rollers.
- Dieelectric -and IR heating are the best dry method for impregnated latex fibre structures.

8.2 Recommendations

Chemist should be involved in further research

- latices must be 'designed' to fulfill the function of matrix in a composite material.
- Influence of latex components on composite characteristics should be determined.
- Emulsion sizings for ABS (i.e. MAABS) and acrylics must be obtained or 'designed'.

Different drying methods must be tested

- Drying speed of impregnated mats using different drying methods must be determined.
- Costs of different methods must be determined.

More testing required

- Tensile and impact properties must be determined.
- Effect of other sizings on mechanical properties must be determined.
- Different natural fibre mats must be tested.

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Appendix A

Natural fibre cultivation areas and quantities

Cultivation areas and fibre quantities produced in the EU, economic year 1999/2000 (Source: EU 1999a and b, supplemented by nova Institute)

EU Member Country	Cultivation Area		Production Area		Fibre Yields			Production		
	Flax	Hemp	Flax	Hemp	Flax Long Fibres	Flax Short Fibres	Hemp Short Fibres	Flax Long Fibres	Flax Short Fibres	Hemp Short Fibres
	ha	ha	ha	ha	tonnes[1] /ha	tonnes/ ha	tonnes/ ha	tonnes/ year	tonnes/ year	tonnes/ year
Belgium	12,199	-	11,500	-	1.20	0.90	-	13,800	10,350	-
Denmark	32	23	30	20	-	1.20	1.50	-	36	30
Germany	569	4,003	500	4,000	-	1.20	1.50	-	600	6,000
Greece	-	-	-	-	-	-	-	-	-	-
Spain	126,226	13,473	25,000	5,000	-	0.60	0.75	-	15,000	3,750
France	48,000	10,500	46,500	10,000	1.20	0.90	1.95	55,800	41,850	19,500
Ireland	-	22	-	20	-	0.60	1.05	-	-	21
Italy	-	197	-	190	-	-	0.75	-	-	143
Luxembourg	-	-	-	-	-	-	1.50	-	-	-
The Netherlands	3,568	872	3,568	872	1.20	0.90	1.95	4,282	3,211	1,700
Austria	336	289	336	289	-	1.20	1.30	-	403	376
Portugal	-	-	-	-	-	0.60	0.75	-	-	-
Finland	863	93	863	93	-	1.20	1.15	-	1,036	107
Sweden	1,327	-	1,000	-	-	1.20	-	-	1,200	-
U.K.	15,000	2,500	15,000	2,500	-	0.60	1.05	-	9,000	2,625
Total	208,120	31,972	104,297	22,984				73,882	82,686	34,252

Appendix B

Current natural fibre prices

Market prices of flax and hemp short fibres and competitive fibres. Germany 1999 and 2000

Natural fibre and application	Price in DM/kg
Flax fibres from EU, inferior quality, uncleaned for commodity pulp (shives content up to 50%)	starting at 0.20
Flax fibres from EU, for specialty pulp (shives content 10–25%)	0.50–0.60
Flax long fibre tow from Eastern Europe	starting at 0.70
Flax fibres from EU for floor sound insulation	0.80–0.90
Flax fibres from EU for composites	0.90–1.05 (02/2000: up to 1.30)
Flax fibres from EU for thermal insulation materials	0.90–1.10 (02/2000: up to 1.30)
Flax long fibres from EU for apparel	2.50–4.50 (some higher)
Hemp fibres from EU for specialty pulp (hurds content 10–25%)	0.55–0.70
Hemp fibres from EU for floor sound insulation	0.85–0.90
Hemp tow from Eastern Europe (good quality, 1998)	about 1.00
Hemp fibres from EU for composites	0.90–1.20
Hemp fibres from EU for insulation materials	0.90–1.20
Hemp long fibres from Eastern Europe (1998)	2.00–6.00 (some higher)
Chemically and enzymatically retted hemp fibres for apparel industry (3 qualities, China 1998)	3.00–7.00
Jute fibres new (Bangladesh) for composites	1.10–1.20
Jute fibres new (Bangladesh) for specialty pulp	0.80–0.90
Sisal new (Africa and South America) for composites	1.10–1.45
Sisal new (Africa and South America) for specialty pulp	1.10–1.20
Kenaf new (Bangladesh) for composites	1.05–1.20
Kenaf new (Bangladesh) for specialty pulp	0.90–1.00
Abaca (Philippines) for specialty pulp	1.60–1.80
Cocos fibres for geotextiles	0.40–0.60
Cocos fibres premier quality	0.70–0.80

nova 2000

Sources: BOHNDICK 1999, DAENEKINDT 1999, FRANK 1999, GÜTHE 1999, HENDRIKS 1998, HOLLER 1998, LANIUS-HOMANN 1998, KASSE 2000, KINKEL 1999, KÖRNER 1999, NOVA 1999, NOVA 2000, VLASBERICHTEN 2000

Appendix C

Use of natural fibres in automotive parts

Use of natural fibres in automotive parts (Source: SEURIG-FRANKE 1999, STROBEL 1999, OPEL 1999, ENERGIEPFLANZEN 1999, THE TEXTILE CONSULTANCY 2000)

Manufacturer	**Model** Application (dependent on model)
Audi	**A3, A4, A4 Avant, A6, A8, Roadster, Coupe** Seat back, side and back door panel, boot lining, hat rack, spare tire lining
BMW	**3, 5 and 7 Series and others** Door panels, headliner panel, boot lining, seat back
Daimler/Chrysler	**A-Series, C-Series, E-Series, S-Series** Door panels, windshield/dashboard, business table, pillar cover panel
Fiat	**Punto, Brava, Marea, Alfa Romeo 146, 156**
Ford	**Mondeo CD 162, Focus** Door panels, B-pillar, boot liner
Opel	**Astra, Vectra, Zafira** Headliner panel, door panels, pillar cover panel, instrument panel
Peugeot	**New model 406**
Renault	**Clio**
Rover	**Rover 2000 and others** Insulation, rear storage shelf/panel
Saab	Door panels
SEAT	Door panels, seat back
Volkswagen	**Golf A4, Passat Variant, Bora** Door panel, seat back, boot lid finish panel, boot liner
Volvo	**C70, V70**

Appendix D

Determination of latex solid content

Solid content of AN12DE and ABS lattices were determined by weighing:

An empty dish	(A)
Dish filled with latex	(A+B)
Dish with dried latex	(A+C)

Solid content can now be calculated using the following equation:

$$\frac{(A+C)-A}{(A+B)-A} \ast 100\ [\%]$$

The results of this procedure are given in table A1

Latex type	**ABS**	**Acronal 12 DE**
A	65.4680	64.7251
A+B	75.5005	76.6743
A+C	68.1499	69.4842
Solid content	26.7%	39.83%

Table A1: Latex solid content

Appendix E

Determination of latex particle density

The first step in determining the specific weight of latex particles is the processing of a solid latex sample. This is done in the following procedure:

1. Latex is poured in a deep glass dish.
2. Air is released from the latex in the dish in a vacuum oven.
3. Latex is put in a hot air oven and dried for several hours.
4. Dry latex particles are removed from the dish and pressed in a mould.
5. A material sample is cut from the latex plate that was pressed in step 4.

This procedure is followed by a hydrostatic density measurement on the sample using the setup shown in figure B1.

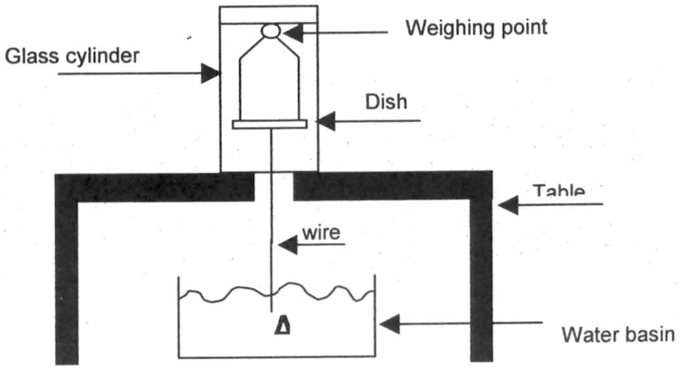


Figure B1: Hydrostatic density measurement setup

The different steps in the measurements are:

Dry weighing of the wire by attaching it to the dish (B1).
Wet weighing of the wire attached to the dish and partly submerged in the basin (B2).
Dry weighing of the wire and the material sample together (B3)
Wet weighing of the wire and the material sample together, and the sample totally submerged in the basin (B4).

The temperature of the water in the basin is 20.6 °C. This corresponds to a water density of 999.078 kg/m^3. Finally the latex particle density can be calculated using the following equation:

$$0.999078 * \frac{1}{1-\frac{(B4-B3)}{(B3-B1)}}$$

The results of the measurements for ABS and Acronal 12DE are given in table B1

Material	**ABS**	**Acronal 12DE**
B1 [gr]	0.7033	0.7033
B2 [gr]	0.6000	0.6000
B3 [gr]	3.8519	2.4252
B4 [gr]	0.6170	0.8323
Density [gr/dm^3]	1003.496	1153.726

Table B1: hydrostatic measurement results

Appendix F

How to apply the right amount of latex on the flax mat

Composite mechanical properties are mainly determined by fibre content, therefore, good control over fibre content in prepreg processing is essential.

In the experiments described in chapters 4, 5 and 6, the amount of latex that had to be deposited on the fibre mat was determined using equation F.4, that will be derived in the following:

Volume of the fibres to be impregnated (V_{fibres} [cm^3]) is calculated using:

$$V_{fibres} = \frac{M_f * (1 - W_c)}{\rho_f} \qquad \text{Equation (F.1)}$$

In which:

M_f = fibre weight (not dried) [g]

W_c= water content in the fibres

ρ_f = specific weight of flax fibre [g/cm^3]

Volume of the dried latex deposited on the fibres (V_{matrix} [cm^3]) is calculated using:

$$V_{matrix} = \frac{M_l * \phi}{\rho_m} \qquad \text{Equation (F.2)}$$

In which:

M_l = weight of latex deposited [gr]

Φ = latex solid content (see appendix ()) [kg/kg]

ρ_m= specific weight of dried latex (see appendix ()) [gr/cm^3]

Equation (1) and (2) are used to calculate the fibre volume content in the final composite (V_f [%]):

$$V_f = 100 * \frac{V_{fibres}}{V_{fibres} + V_{matrix}} \qquad \text{Equation (F.3)}$$

Equations (2) and (3) show that V_f can be regulated by adjusting M_l (deposit more or less latex on the fibres) or Φ (by adding water to the latex).

Substitution of equation (1) and (2) in equation (3) and rearranging yields:

$$M_l + M_f = \underbrace{\left[1+\frac{(1-V_f)*W_c*\rho_m}{V_f*\phi*\rho_f}\right]}_{\mathbf{C}} * M_f \qquad \text{Equation (F.4)}$$

In practice, the procedure for depositing the right amount of latex is as follows:

1. Determine the weight of a piece of flax mat (A)
2. Calculate factor C (equation F.4)
3. Impregnate the mat to a total weight of C times A

In calculating factor C, two assumptions were made:

- The specific weight of flax fibre (ρ_f), is 1.5 gr/cm^3. This value was taken as an average from the values given in literature and not determined by testing.
- Water content of flax fibre (W_f) was taken constant, namely 10%. This percentage was found in earlier work on the same mat material []. Because W_f depends on humidity, the use of a fixed value can lead to a deviation between actual and calculated fibre weight. All the laminates that were compared however, were impregnated on the same day and. For this reason, the deviation will be the same for all laminates.

Appendix G

Flexural test method

Test standard

Flexural properties of thee laminates produced in this research were tested using test standard ISO 178; 1993(E), a three points bending test. A rectangular shaped specimen is supported at the ends and loaded at midspan (see figure G 1).

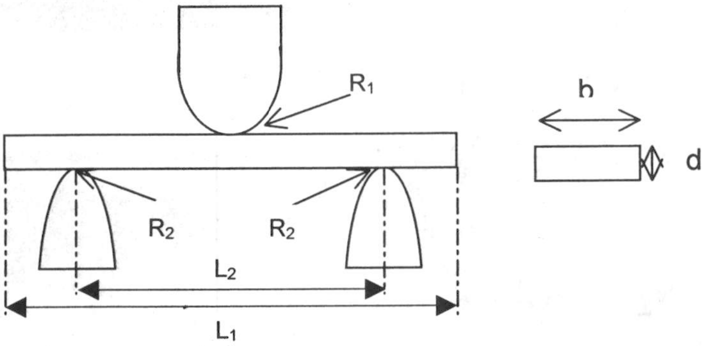


Figure G 1: Position of the test specimen at the start of the test

Test equipment

All tests have been done on a Zwick 1455. Test speed was 2mm/min

Shape of test specimen

Test specimen had a rectangular crosssection with b = 15mm and d between 2 and 3 mm, depending on the fibre volume of the laminate. Span length (L_2) was 16 times d and the total length (L1) 20 times d. The radius of the support (R_2) was 3 mm and the radius of the loading nose was 3.2 mm.

Flexural properties calculation

The Zwick test test equipment measures the force applied at midspan and the deflection at the same position. These two values are introduced in the formulas for stess and strain that are valid for the three point bending test, were the load is applied at midspan:

$\sigma_{flexural}=3PL/2bd^2$;   and

$\varepsilon_{max\ flex} = 6ld/L^2$

with :

$\sigma_{flexural}$ = maximum flexural stress

P = apllied force at midspan

L_2 = span length

b = width

d = thickness

l = deflection at midspan

Questions:

1) ~~Hoe~~ Je wilt dan de latex er bovenop in hout te zetten.

wat betekend dat voor —

- interactie deeltjes <-> folie
- architectuur v/h vezelpakket

2) hoe werkt het mapp nu precies.

- bevochtiging
- hechting
- etc

3) hoe thermo formable zijn deze composieten. t.o.v glas/th pl.

- interlaminar fraction.
- etc.

~~1) Zo kunnen geen mogelijk [illegible]~~

→ II 2) Hoe werkt het mapp eigenlijk – bevochtigen – hechting,

→ II 3) Wat zou het meest geschikte materiaal zijn om de MATRIX te gebruiken? → water bevochtigbaar.
→ siliconen
→ latex + pol
→ stabilisering.
?

4) hoe groot vloer voorwaarde?

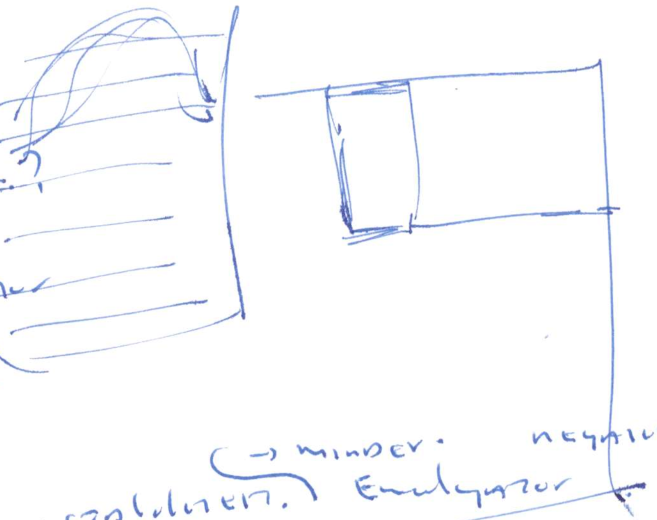
~~5) Wat is de WERK toepassing. [illegible] maal.~~

→ II 6) Thermo formalisering, verder processing.

II 7) voorbehandelen vlas.

II 8) hoe je met koeling de deeltjesverandering?

⇒ 9) mapp als stabilisator van pp composiet?



→ minder. negatief.

→ automobiel industry. → stabilisator. Emulgator

→

Destabilisator in de map.

→ hoe je het in de matrix bijmengen.

Stoffenhouding voor droging.